Light-Matter Interactions in Low-Dimensional Materials

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Light-Matter Interactions in Low-Dimensional Materials

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Structured Electromagnetic Materials Group
DTU Fotonik

March 31, 2019
The thesis you are about to read is the culmination of my three years as a PhD student in the Structured Electromagnetic Materials group at the Technical University of Denmark (DTU). Contained herein is a compilation of the results obtained from the research projects I have been involved in during these three years. The projects have been focused on experimental characterisation of the optical properties of plasmonic structures and two-dimensional (2D) materials, and especially how we can tailor these properties.

We begin with an introduction to the optical properties of metals. This leads us to the concept of collective electron excitations called plasmons. We especially focus on the localised surface plasmons hosted by nanoscale metallic structures, and we review their properties in single and coupled configurations. We conclude this part with a presentation of the experimental investigation into the interaction between spherical gold nanoparticles and single-crystalline gold substrates, which are known to host electronic surface states. We detect no change, however, in the optical properties from these states, when we compare to a polycrystalline reference substrate. We ascribe this to the weak effect induced by the surface states compared to other factors such as the surface roughness.

Following this, we introduce the family of 2D materials known as the transition metal dichalcogenides (TMDCs). We review their basic electronic and optical properties, and we explore the strong light-matter interaction in these atomically thin materials dominated by electron-hole complexes known as excitons. We also see how it is possible to theoretically model the optical response of such a 2D material on a substrate with the transfer-matrix method, and we use this to extract the dielectric permittivity of WS$_2$ mono- and multilayers.

Having the basic theory in place, we demonstrate how it is possible to manipulate the emission energy of excitons in WSe$_2$ monolayers, encapsulated between flakes of hexagonal boron nitride (hBN), by nanostructuring the dielectric environment. This is explained by the reduced binding energy of the excitons from the dielectric screening, and the change in the material band structure from the presence of the hBN. We find that the emission energy increases with decreasing screening from the hBN, an effect that appears to be dependent on whether the metal atom is molybdenum or tungsten.

We then move on to discussing the coupling of emitters and cavities in the weak- and strong-coupling regimes. The emitters are here represented by the excitons in
TMDCs, and the cavities are plasmonic structures. In the case of weak coupling, we report photoluminescence quenching in MoS$_2$ when coupled to semi-continuous, thin gold films, known as percolation films. This quenching is ascribed to the introduction of nonradiative pathways by the percolation film. We furthermore show a 50% reduction in the reflected signal, which could stem from enhanced absorption in the MoS$_2$ layer, since we observe a drastically different response without the presence of the 2D material.

We then continue to discuss the basic theory of strong coupling, after which we present the experimental confirmation of strong coupling for mono- and multilayers of WS$_2$ coupled to ultra-thin, single-crystalline gold nanodisks. In the monolayer case, we explore this coupling both in scattering and reflection measurements, where we argue that the latter is representative of the absorption properties of the coupled system. For the multilayer, we show a record-high figure of merit for our system consisting of an open plasmonic cavity coupled to a TMDC. We conclude the chapter by briefly exploring the temperature dependence of the optical properties of such a system.

Finally, a summary and ideas for future work is provided. Since an outlook is given for the individual projects as they are presented, the outlook is comprised of my thoughts on how to continue the work presented here, if more time was available.
Afhandlingen, du skal til at læse, er kulminationen på mine tre år i gruppen Strukturerede elektromagnetiske materialer på Danmarks Tekniske Universitet (DTU) som ph.d.-studerende. Indeholdt heri er en samling af de opnåede resultater fra de forskningsprojekter, jeg har været involveret i over disse tre år. Projekterne har været fokuserede på eksperimental karakterisering af de optiske egenskaber af plasmoniske strukturer og todimensionelle (2D) materialer, og især hvordan vi kan tilpasse disse egenskaber.


Herefter introducerer vi familien af 2D-materialer kendt som overgangsmetaldichalcogenider (TMDC’er fra engelsk). Vi gennemgår deres basale elektroniske og optiske egenskaber, og vi undersøger den stærke interaktion mellem lys og fast stof i disse atommetynde materialer, som er domineret af elektron-hul komplekser kaldet eksitoner. Vi ser ydermere, hvordan det er muligt teoretisk at modellere den optiske respons af et sådant 2D-materiale på et substrat med transfermatrix-metoden, og vi benytter denne til at bestemme den dielektriske permittivitet af WS$_2$ mono- og multilag.

Med den grundlæggende teori på plads demonstrerer vi, hvordan det er muligt at manipulere emissionsenergien af eksitoner i WSe$_2$ monolag, indkapslet mellem flager af hexagonal bor-nitrid (hBN), ved at nanostruktrue den dielektriske miljø. Dette bliver forklaret med, på den ene side, den reducerede bindingsenergi af eksitonerne grundet den dielektriske skærmning, og på den anden side ændringen i materialets båndstruktur fra tilstedeværelsen af hBN’et. Vi konkluderer, at emissionsenergien øges ved formindsket skærmning fra hBN’et, en effekt der ser ud til at være afhængigt af, om metalatomet er molybdæn eller wolfram.

Vi bevæger os dernæst over i en diskussion af kobling mellem lyskilder og kaviteter i regimene for svag og stærk kobling. Lyskilderne er her eksitoner i TMDC’er, og

Vi fortsætter derefter med at diskutere den basale teori for stærk kobling, hvorefter vi præsenterer den eksperimentelle eftervisning af stærk kobling for mono- og multilag af WS$_2$ koblet til ultratynde, monokrystalline nanodiske af guld. I tilfældet med monolag udforsker vi denne kobling både i sprednings- og reflektionsmålinger, hvor vi argumenterer for, at den sidstnævnte er repræsentativ for absorptionsegenskaberne af det koblede system. For multilag præsenterer vi en rekordhøj præsentationsparameter for vores system bestående af en åben plasmonisk kavitet og en TMDC. Vi afrunder kapitlet med kortfattet at undersøge temperaturafhængigheden af de optiske egenskaber af et sådant system.

Slutteligt gives en opsummering og ideer til fremtidigt arbejde. Eftersom en diskussion af disse bliver givet sammen med de individuelle projekter, består fremtidsperspektivet af egne tanker om, hvordan det videre arbejde med resultaterne præsenteret heri kunne fortsætte, hvis mere tid var til rådighed.
List of Publications

Included in this thesis

Journal publications


Accepted


Additional work

Journal publications


Conference contributions


**Submitted**


  – Submitted to Nature Communications, back from first round of review, major revisions.


  – Submitted to Chemistry of Materials, in second round of review, minor revisions.
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Introduction

Controlling the interaction between light and matter is crucial to the workings of modern-day society. Harvesting clean and renewable energy using solar cells, transporting massive amounts of data in optical fibres, unveiling the secrets of the far reaches of space, but also of the smallest man-made structures in nanofabrication; all of this is made possible by the use of light in various forms. The important role filled by optics and photonics in the world around us was recognised in 2015, where the United Nations declared the International Year of Light. However, just because we are no longer in the official Year of Light, researchers around the globe have by no means slowed their pursuit of fundamentally new ways to solve the problems of today and tomorrow using electromagnetic radiation.

A revolutionary new avenue was opened with the successful isolation of graphene in 2004 by Novoselov and Geim [1]. This monolayer of carbon atoms, which was previously used only as a theoretical model system for graphite and carbon nanotubes, was suddenly shown to be thermodynamically stable at ambient conditions despite its two-dimensional (2D) nature. Since then, graphene has seen an ever-increasing research interest, which quickly spread to other materials with the realisation that these could also be isolated in monolayer form. These materials have the strong in-plane bonds in individual layers, as well as the much weaker out-of-plane Van der Waals-bonds between layers, in common. But the more we learn about these new material platforms, the more we realise that the diversity is equally as large as the similarity. Since more than 1000 materials have been now predicted to exist in a 2D phase [2], the toolbox in nanoscale materials science has been greatly expanded over the past decade, and this development is heralded to have a profound impact across scientific disciplines.

From the view of nanophotonics, these materials have the potential to revolutionise how we are able to fabricate and integrate optical devices. In Figure 1.1 we see that with just four different materials, we can cover most of the electromagnetic spectrum from the ultraviolet to radiowave frequencies. One family of materials in particular has received enormous research interest, namely the transition metal dichalcogenides (TMDCs) represented by MoS$_2$ in the Figure. The TMDCs are semiconductors with varying bandgaps, which allows them to cover the visible and near-infrared spectrum. This makes them particularly interesting for technological applications, as they can potentially replace the usual 3D semiconductors such as Si or GaAs. In electronics, the strain tolerance of these materials can lead to flexible, wearable devices as well as solar cells and light emitting structures [4–6]. The latter is a result
Chapter 1. Introduction

Figure 1.1: Overview of the electromagnetic spectrum and the spectral range covered by different two-dimensional materials from insulator to semimetal. Figure from [3].

of the strong interaction of the TMDCs with light [3], where e.g. a single, atomically thin layer of MoS$_2$ can absorb 5.5% of incoming light in the visible spectrum [6]. This is facilitated by the 2D dimensionality, as it enhances physical phenomena such as electron-hole complexes, known as excitons, which in traditional semiconductors are only stable at cryogenic temperatures [7, p. 95-101]. However, due to the reduced Coulomb screening in the 2D materials, the excitons have binding energies of several hundred meV [8], and as such play an essential role in the optical properties of the TMDCs also at ambient conditions.

In recent years, the 2D excitons have seen increasing interest for use as potential replacements for typically used quantum emitters such as quantum dots or nitrogen-vacancies in diamonds. This interest is spurred by the stability of the excitons at room temperature, as well as the ability to engineer their properties through e.g. strain [9], gating, temperature [10], or even by combining different 2D materials in Van der Waals-heterostructures [11–16]. Since the 2D materials by nature are almost purely a surface, they are furthermore strongly influenced by their surroundings both in passive form from changing the dielectric environment [17, 18], but also more actively by using various photonic cavities. This integration of TMDCs into cavities is relatively straightforward because of their strong optical response and small physical footprint.

The first realisations of this integrations were in dielectric cavities [19, 20], but these are limited in their miniaturisation potential by the diffraction limit. This limit can
be overcome by using localised surface plasmons, collective electron oscillations hosted by nanoscale metallic structures. The losses associated with plasmons has previously hindered applications in nanophotonics, but the strong field enhancement and accompanying confinement of the electromagnetic field to the nanometer scale can overcome these losses when coupled to emitters. This coupling can exist in two regimes, the weak and the strong.

Although the weak coupling does not change the resonance energy of the emitter significantly, it can greatly modify the absorption and emission properties e.g. in the form of the Purcell enhancement [21, 22], and this has already found widespread application in for instance photovoltaics, lasers [23], and efficient single-photon sources [24].

The strong-coupling regime, on the other hand, leads to profoundly new states that are neither light nor matter, but a mix of the two. These exotic states have yet to find commercial applications, in part since the realisation of strong coupling was previously restricted to cryogenic temperatures [25, 26]. Although room temperature strong coupling has been achieved using different organic dyes [27, 28], these have a tendency to bleach and degrade over time. The TMDCs, on the other hand, have increased longevity [29], which allows for integration into devices that could allow for real-world applications in areas such as integrated optical devices, quantum information processing, and low-threshold lasers [23].

In this thesis we study the optical properties of both plasmonic structures and excitons in TMDCs, and especially what happens when we start combining these two physical excitations, as described in the following.

### 1.1 Outline

We begin this thesis by introducing the necessary concepts concerning the interaction of light and matter to understand the results reported herein. Chapter 2 presents the experimental techniques used in this work, along with a description of how the measurements were performed and the subsequent data processing.

Chapter 3 gives an overview of the optical properties of metals, starting with the simple Drude model and its uses and limitations. Following this, we take a look at the phenomenon of plasmons especially in the case of localised surface plasmons hosted by small, metallic structures. This leads us to the experimental results obtained in the investigation of surface states in single-crystalline gold substrates, more specifically their impact on the optical response of metallic nanoparticles resting on such a substrate.

In Chapter 4 an introduction to the field of 2D materials in the form of the TMDCs is given. We start with an overview of the electronic structure, which will subsequently be used to understand the surprisingly strong optical response in both absorption and emission of these atomically thin materials. These properties are to a large extent due to the presence of electron-hole complexes (excitons), which play a significantly greater role than in classical 3D semiconductors.

We continue in Chapter 5 by applying this to the case of bandgap engineering of the TMDCs by nanostructuring the dielectric environment. Specifically, we investigate the effect of encapsulating WSe$_2$ in hexagonal boron nitride, where one side has been nanostructured with an antidot lattice, by looking at the dependence of the emission spectrum on the morphology of the dielectric environment.
The main results of the thesis based on the results in the two attached papers are presented in Chapter 6. Here we review how an emitter couples to a cavity in the weak- and strong-coupling regimes, and results from both coupling regimes are reported. The weak coupling is investigated in semi-continuous gold films deposited on MoS$_2$, where we show the influence of the metallic structures on both absorption and emission in these structures. The case of strong coupling is represented by single-crystalline, ultra-thin gold nanodisks coupled to WS$_2$ mono- and multilayers. The clear presence of the strong-coupling regime is presented in both systems, where we see a significant increase in the system figure of merit when changing to the multilayer configuration.

Finally, a summary of the main experimental findings presented in this work is given, followed by an outlook towards future work which could be undertaken to utilise the strengths of the obtained results.
In order to understand the data presented in this thesis, it is important to know how that data is obtained and processed. In this chapter a brief introduction to the experimental set up is given, along with an introduction to the three most common measurement techniques used in this work, namely white-light brightfield and darkfield as well as photoluminescence spectroscopy. Following this is a description of how data was acquired and post-processed. As a note, the procedures described here are all in a reflection geometry.

2.1 The set up

The experimental set up used for all of the measurements presented in this thesis is based on a confocal Nikon Ti-U Inverted Microscope. At the start of this PhD work, the microscope was only equipped with white light sources and had a manual mechanical stage which complicated precision measurements on the micrometer scale. Significant work has gone into extending the capabilities of the set up and easing experimental procedures to allow for a wider range of available measurements in a more accessible and reproducible manner.

The set up has been extended with an electronically controlled XYZ-stage with electromagnetic stepper motors in the XY-direction and a piezoelectric motor in Z. The stage has excellent precision in all directions (resolution $\sim 100$ nm in XY, 0.4 nm in Z). It is furthermore programmable allowing for automated spectral maps and measurements which can also include focus sweeps. Additional light sources have also been introduced in the form of two diode lasers: One with a centre wavelength at 407 nm (3.048 eV), and one at 520 nm (2.375 eV). The simplest and most frequent use for these are photoluminescence measurements, but as they are free-space coupled into the microscope, manipulation of the light in the form of e.g. polarisation is possible. The modularity offered by free-space coupling also enables further upgrades in the future for doing more exotic measurements, possibly with other light sources.

For obtaining spectra, the microscope is connected to a Shamrock 303i Spectrometer equipped with an electronically cooled Newton 970 EMCCD. A connector arm from the microscope to the spectrometer focuses the image on an input slit, which allows for precise selection of the collection area. The 2D nature of the CCD additionally opens for the choice of which spectrometer lines to include in the final spectrum.
Chapter 2. Experimental Techniques

2.2 Experimental techniques

2.2.1 Darkfield

Darkfield (DF) microscopy is a well-established technique in the optics community. Instead of using light focused through the lens system in the objective, a beam block is used to remove the centre part of the incident beam. The light is then led through an outer ring in the objective to a mirror surrounding the lens causing the light to impinge on the sample at a high angle (typically > 50°), see Figure 2.1. The large incident angle prevents direct reflections into the collection lens, thus leaving only light scattered off the sample to enter the detection system. This results in an image as the one in Figure 2.2a where we see spherical gold particles with a radius of 80 nm on a glass substrate. Here, the origin of the technique’s name is also clearly exemplified with the bright particles on a dark field. Ideally, DF images would lead to a flat substrate appearing completely black and all scattering objects showing clearly on the dark background. A real experiment is far from ideal, however, and as such removal of the background signal is crucial to obtain only the desired spectrum, especially if the object under investigation is close to a strong scatterer such as a material edge.

If the signal of interest can be isolated from the background noise, the major strength of DF microscopy is immediately obvious: The measured physical parameter is only the scattering cross section, $\sigma_{\text{scat}}$, of the structure in its environment. The scattering cross section has an angular dependence, and therefore a typical measurement does not give the full $\sigma_{\text{scat}}$, but only the part collected by the numerical aperture.

Combined with the resolution of the stage this results in micrometer precision control of the XY collection area (cf. Figure 2.5).

For more information about the set up, see Appendix A.

Figure 2.1: (a) Sketch of darkfield illumination on a sample (yellow) and collection of the scattered light (red). (b) Top: The bottom of a darkfield objective showing the outer hollow ring (red) and the inner core containing the imaging lenses (blue). Bottom: Top view of a darkfield filter cube showing the mirror (red) and the hollow centre (blue).
2.2. Experimental techniques

of the objective. To get the full, an integration sphere would have to be used. The scattering cross section has units of an area, and can be understood as the virtual size of the structure as seen by an incoming electromagnetic field. The parameter $\sigma_{\text{scat}}$ can furthermore be calculated from both analytical and numerical models allowing for direct comparison between experiments and theory often with very good agreement [30, 31]. Normally, only qualitative agreement is obtained, but by using a spatial modulation technique, it is also possible to measure the absolute value of $\sigma_{\text{scat}}$ with excellent quantitative agreement [32].

![Image of spherical gold nanoparticles with a diameter of 80 nm on a glass substrate in (a) darkfield and (b) brightfield.](image)

**Figure 2.2:** Image of spherical gold nanoparticles with a diameter of 80 nm on a glass substrate in (a) darkfield and (b) brightfield.

2.2.2 Brightfield

Brightfield (BF) microscopy is the technique that most people associate with optical microscopy. Light is directed towards the sample using a beamsplitter, where it is focused by an objective. The reflected part is then recollected by the objective and travels along the same beam path through the beamsplitter, after which it is directed towards the spectrometer; the process is sketched in Figure 2.3.

In general, the relation $R + T + A = 1$ holds, i.e. that all the incoming light is either reflected ($R$), transmitted ($T$), or absorbed ($A$), respectively. What constitutes the reflected signal, however, depends on the sample in question. A thing to note is that the expression $R = 1 - T - A$ implies that the reflected signal is convoluted with the transmission and absorption of the sample in question. In the case of a continuous film, measuring the BF reflection and transmission of a semi-transparent sample is relatively straightforward, from which the absorption can be inferred. For nanostructures, however, the incoming light is scattered instead of being directly reflected, which happens because of their small size typically below the diffraction limit. One therefore has to be wary of directly comparing the reflection and transmission to e.g. the scattering cross section, since the relation between them can be non-trivial\(^1\). As we shall see in Section 6.3.4, however, it is sometimes possible to infer the absorption

\(^1\)Indeed, light scattered from a nanostructure also has an angular dependence, and as such both the transmitted and reflected signal will contain a portion of the light scattered in the forwards and backwards direction, respectively.
properties for a non-transparent sample \((T = 0)\), although this is still only an indirect measure. In order to determine the absorption independently, special measurement techniques are required \([32, 33]\).

A BF image of the same particles as in Figure 2.2a is shown in Figure 2.2b. A portion of the light is Fresnel reflected at the air/glass interface, where the additional light backscattered from the particles gives rise to the contrast difference. Since the particles are well below the diffraction limit (being only 80 nm in diameter), background removal would also here be necessary to isolate the nanoparticle signal as in the case of DF.

2.2.3 Photoluminescence

Photoluminescence (PL) is the general name for light emission from matter after photoexcitation, i.e. absorption of photons. Exactly what gives rise to the absorption and following emission depends on the sample in question. Common sources are excitons in semiconductor quantum dots, luminescent defect states e.g. in diamond, and in more recent years also excitons and defect states in two-dimensional materials.

The simplest way to probe these luminescent states is to use a continuous wave laser with an energy larger than the transition in question. The light is guided to the sample and focused to a small spot size, whereafter the re-emitted light is collected in the same configuration as in BF (cf. Figure 2.3). The excitation area is usually determined as the first null of the Airy disk, which has a diameter of

\[
d = \frac{1.22\lambda}{\text{NA}},
\]

where \(\lambda\) is the excitation wavelength, and NA is the numerical aperture of the objective. Using the blue laser at 407 nm and an objective of 0.9 NA results in a spot size of \(d = 552\) nm.

To understand the physical process behind PL, we use a simple two-band system. An impinging photon will promote an electron to the conduction band. The electron (hole) then relaxes to the bottom (top) of the conduction (valence) band through
2.3. Data processing

As described above, post-processing of the data is to some extent always necessary in order to extract the real spectrum from the raw experimental data. The CCD itself gives 200x1600 data points for a single acquisition, where each of the 200 lines corresponds to a spectrum in the selected wavelength range. However, due to the finite size of the studied object (and often also the diffraction limit), the spectrum from e.g. a nanoparticle will extend over multiple of these lines, see Figure 2.5c. The raw data, $I_{\text{raw}}$, is then comprised of a sum of the spectra from the relevant CCD lines. The spectral shape of $I_{\text{raw}}$ is, besides the spectrum of interest, influenced by three sources described in the following:

$I_{\text{dark}}$

Although the CCD is electronically cooled, thermal excitations of carriers is still possible due to the low bandgap of silicon (1.14 eV at room temperature). Each of these excitations will result in a signal, in the same manner as impinging photons, and...
are called dark counts (since they are present even without incident light). How-
ever, as the thermal excitations are statistical in nature, they are fairly constant over
time and as such give rise to an almost static addition to the overall signal intensity
independent of the position on the CCD and thus on the wavelength.

$I_{bg}$

Since it is nearly impossible to completely isolate an object from other sources of
light, removal of background light is paramount to obtaining the pure signal from
the structure under study. The term “background” here covers many things, e.g.
stray light in the set up from light leakage of the lamp and room, scattering from
other nearby sources such as edges and large particles, but also substrate effects
in reflection mode when measuring nanoscale structures. Since the CCD simultane-
ously obtains spectra all along the slit (cf. Figure 2.5b-c), a separate background mea-
surement is not necessary. Instead, the background signal can be directly obtained
from the close proximity of the object under study, which ensures the determined
background is as close to the real one as possible.

$I_{ref}$

When doing white-light spectroscopy, it is very rare to have an excitation source with
a uniform spectral distribution over the energy region of interest. Instead, the source
usually has a distinct profile (e.g. a halogen lamp resembles a Planck curve for black-
body radiation), which has to be corrected for. Since we are only interested in the
the spectral profile, the reference spectrum is normalised to its maximum value.

Taking all of the above into account, the real spectrum $I_{spec}(\lambda)$ can then be found as

$$I_{spec}(\lambda) = \frac{I_{raw}(\lambda) - I_{bg}(\lambda) - I_{dark}}{I_{ref}(\lambda)}.$$  \hspace{1cm} (2.3.1)

A summary of the entire process of data acquisition and post-processing can be seen
in Figure 2.5. All white-light (DF and BF) microscopy spectra shown in this work
has undergone the data processing described above.

For the PL spectra the situation is different. Since we are using local illumination
with a diffraction limited spot size, the sample region giving rise to a signal is also
limited, and the background should therefore be zero. Although stray light from the
surroundings could still influence the measurements, this can be minimised during
acquisition (the largest contributor is normally the white-light source, which is not
used for PL measurements). Furthermore, since we are probing the emission proper-
ties at lower energy than the excitation source, the spectral distribution of the source
does not influence the CCD response, and therefore $I_{ref} = 1$ for all wavelengths. As
such, $I_{spec} = I_{raw}$ (after the subtraction of dark counts), and the CCD signal can often
be used as is.

### 2.3.1 Spectrum background removal

Throughout the duration of this PhD, a tremendous amount of work has gone into
understanding the set up and how to remove potential artefacts from the acquired
data. Many steps can be taken in the measurement process both on the sample and
set up side, and these will naturally be dependent on the specific implementation.
Some generally applicable conclusions on how good spectra can be obtained can
2.3. Data processing

![Figure 2.5: Process flow of data acquisition and processing. A region from the real-space darkfield image in (a), showing 80 nm spherical gold nanoparticles on glass, is selected using the slit with a width of 150 µm as seen outlined by the white lines in (b). From this, the spectral image in (c) is obtained, where the lines used for the raw signal and the background are indicated in white and blue, respectively. Using Eq. (2.3.1) finally leads to the spectrum shown in (d).](image)

be drawn, however, especially when measuring DF scattering spectra of weak scatterers. The case made in the following is for darkfield measurements, but they are equally applicable to brightfield ditto.

As we see in in Figure 2.5d, the background comprises a significant amount of $I_{\text{raw}}$, and away from the nanoparticle resonance up to 100 % of the signal. The background here is very uniform, however, and as such it can simply be taken as an average of the signal from the regions indicated by the blue lines in Figure 2.5c and corrected for in a straightforward manner. But when the background is non-uniform and exhibits spatial dependence, the process of background correction has to be handled more delicately, and often on a measurement to measurement basis.

One example can be seen in Figure 2.6a, which shows a spectral image of the DF scattering from a gold nanodisk on WS$_2$ (see Section 6.3.2). We here see a case of a non-uniform background signal, as the scattering from the top, which arises from a step edge in the WS$_2$, decreases with the distance to the edge. The intensity along the blue cut line is seen in Figure 2.6b, which clearly shows the sloped background. The difference in the intensity between the two regions marked by the dashed lines, which represent the upper and lower background signals, respectively, can be seen in Figure 2.6c. The spectral profile remains relatively unchanged. Of note here is that the shoulder feature in the raw signal around 2.2 eV is also present in the background signal, and therefore this would remain as an artefact in the spectrum if not correctly accounted for.

Using only the upper background signal would immediately give erroneous results,
Figure 2.6: (a) Spectral image of the scattering from a gold nanodisk on WS$_2$. The strong signal in the higher pixel lines comes from a step edge on the WS$_2$, while the intensity in the middle is from the nanodisk. (b) Cut line of the signal intensity along the blue line indicated in (a), where the signal from the nanodisk is clearly seen on a sloped background. Also indicated by the dashed lines is the pixels used for the raw signal (black), as well as the upper (green) and lower (red) background. (c) Spectra obtained from the CCD output in (a). The raw data is comprised of the signal from the gold nanodisk coupled to the WS$_2$ and an unknown mixture of the upper and lower background signals. The average of the two backgrounds as well as a 1:2 mixture are also shown. (d) The resulting spectrum using backgrounds with an average of the upper and lower background signals, and a weighted contribution from the two.
as a large part of the spectrum above 2 eV yields negative counts. Using instead only
the lower background signal would result in spectral artefacts in the final spectrum
in the form of the mentioned shoulder feature. In the spectral image in Figure 2.5c,
the observed uniform background allowed for an even weight between the upper
and lower contribution to the background signal. Applying this method in the
case of the nanodisk yields an incorrect spectrum as shown by the purple line in
Figure 2.6c as well as in the resulting spectrum plotted in red in Figure 2.6d, where
we see negative intensities above 2.1 eV.

If we could approximate the decrease in the scattering intensity from the edge over
the region of the nanodisk signal as linear, we could use the simple average, but
this is clearly not correct. Since the underlying shape of the background intensity is
unknown, it is difficult to find an analytical expression that can reliably estimate the
magnitude in the general case. Furthermore, it is dangerous to base the estimate of
the background on a single cut line, since we are trying to correctly incorporate the
entire spectral range.

In order to remedy this, in this work a weighted average between the two back-
ground contributions has been used on the form

\[ I_{bg} = \alpha I_{bg,upper} + \beta I_{bg,lower}, \]  

(2.3.2)

where \( \alpha \) and \( \beta \) are coefficients that have to be determined for each measurement
individually. The estimation of these coefficients is not trivial, and great care was
taken to avoid introducing artefacts in the spectra. From a theoretical point of view,
analytical or numerical calculations can help in identifying the spectrum from the
background. The 2D nature of the CCD can furthermore aid in determining \( \alpha \) and \( \beta \),
as it allows for direct inspection of the local background and the evolution thereof.
With this it is possible to see the direct impact of systematically varying the regions
and weights for the two components of the background. Furthermore, the spectral
image of the CCD as in Figure 2.6a can be used to identify signal from background,
as we here clearly observe additional intensity below 2.1 eV in the spectra coming
from pixel lines around 120. In this manner, a spectral feature such as the shoul-
der peak at 2.2 eV in Figure 2.6c can be used as a guide to estimate the background
intensity.

Taking these points into consideration, we arrive at the background plotted in or-
ange in Figure 2.6c, where a 1:2 ratio between the upper and lower background sig-
nals has been used, respectively. The resulting spectrum can be seen in the same
colour in Figure 2.6d. We note that in this specific case, the decrease of the back-
ground in Figure 2.6b could be approximated with a power law, but this would then
have to be done on every cut line in the spectrum and an average of these fits would
have to be worked out. Additionally, the method would not be generally applicable,
and as such it has not been pursued further.

It must be emphasised again that great care has to be employed when using the
background in Eq. (2.3.2). Obtaining a representative background is not easy, espe-
cially when the background signal comprises as large a part as is seen in Figure 2.6c,
and user bias can lead to the creation of additional features in the spectra which
are completely unphysical. In general, if there is uncertainty on whether the cor-
rect background can be identified, it is always best to err on the side of caution and
rethink the measurement procedure, or discard the measurement altogether.
Metals have played a key role in human society since we learned the art of metalworking. Historically, they have been highly priced for their durability and strength to create large objects such as weapons and armour, but at the same time also for their ability to make intricately beautiful ornaments and jewellery. The beauty in part comes from the fact that metals achieve a highly reflective surface when carefully polished, which has been used for making mirrors as early as 4000 B.C. [34]. This high reflectivity comes from the metals’ unique optical properties. The first attempt at explaining these properties, however, came millennia later than their use with Paul Drude’s descriptions in 1900 [35, 36]. Drude suggested a kinetic model where free electrons move through the atomic lattice with a characteristic time between collisions with the atoms. We now know that this scattering time is phenomenological and encompasses several other mechanisms as well, but the Drude model still captures the basic observed behaviours for metals, and for this reason it is still used in modern research due to its simplicity.

In this chapter we will start by reviewing the basic properties of a metal, starting from the Drude model followed by extensions of this to better match the observed behaviour of real metals. Having understood the optical properties of metals, we apply these to the case of collective electron excitations known as plasmons. From this we will delve into how particles much smaller than the wavelength of incoming light interacts with the electromagnetic field. Finally, we conclude the chapter with an overview of the experimental endeavours into determining the optical response of gold nanoparticles sitting on highly crystalline gold surfaces, also known as the particle on a mirror-geometry.

3.1 The basics of a metal

When atoms bond to form solids, the electrons in the outermost shells can be distributed in different ways. In most molecules they form covalent or ionic bonds, where the electrons are shared between the atoms, but are otherwise incapable of moving freely. However, for the metal atoms the most energetically favourable configuration is the metallic bond, where a number of ions collectively donate an electron to the lattice, leaving the rigid ions surrounded by a plasma of free-moving electrons. These mobile electrons explain the high conductivity of metals and also
3.1. The basics of a metal

Figure 3.1: Sketch of a simple metal containing one free electron (red) per unit cell, leaving one positive charge in total on the rigid, ionic lattice (green). The electron forms a delocalised plasma shared between the ions (blue).

their strong optical response, as the electrons can quickly respond to incoming electromagnetic fields (the ions can be treated as immobile in the rigid lattice since they are orders of magnitude more massive than the electrons).

What happens when atoms come together to form a solid is that the discrete energy states of the individual atoms hybridise and broaden to form electronic bands. A metal is characterised by having an open Fermi surface, meaning that the most energetic electrons are occupying states in the conduction band. These electrons are the mobile ones forming the plasma described above, while the core electrons occupy the deeper-lying energy states tightly bound to the ions.

3.1.1 The Drude model

In his papers from 1900, Drude envisioned the movement of the free conduction electrons as rigid particles scattering off the immobile ions with a characteristic time scale \( \tau \) between each event [35, 36]. In this picture the differences in conductivity between individual metals can be understood from changes in their electron density \( n \), i.e. the amount of available electrons, and the scattering time. The equation of motion describing the displacement \( x \) of such a free electron with mass \( m_e \) in a driving field of amplitude \( \mathcal{E}_0 \) is:

\[
m_e \frac{d^2 x}{dt^2} + m_e \gamma \frac{dx}{dt} = -e \mathcal{E}_0 \mathcal{E}^{-i\omega t}. \tag{3.1.1}
\]

The damping rate is related to the scattering by \( \gamma = 1/\tau \). For a bound electron we would also have a term proportional to \( x \) akin to a mass on a spring, but the absence of this term indicates the treatment of free electrons with negligible binding to the ions. On the right-hand side of Eq. (3.1.1) is the external electric field driving the movement, which we have assumed to have harmonic time dependence with angular frequency \( \omega \).

By assuming the displacement of the electron to have the same harmonic time dependence, and by considering the total polarisation induced by \( N \) such electrons, we arrive at an expression for the relative dielectric function \( \varepsilon_r(\omega) \) for the metal

\[
\varepsilon_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma}, \quad \omega_p^2 = \frac{Ne^2}{\varepsilon_0m_e}, \tag{3.1.2}
\]
Chapter 3. Optical Properties of Metals

Figure 3.2: Reflectivity at the interface between air and a Drude metal. The values for the damping parameter are given in terms of $\omega_p$.

where $\varepsilon_0$ is the vacuum permittivity, and $\omega_p$ is known as the *plasma frequency*. From this we can see that, in the Drude model, individual metals differ only in terms of two parameters, the plasma frequency and the damping. Although the model is very simple, it gives a surprisingly apt description of metals in many cases.

The reflectivity at an air/material-interface at normal incidence is given by

$$R = \left| \frac{n - 1}{n + 1} \right|^2,$$

Equation (3.1.3)

where $n$ is the complex refractive index of the material. The refractive index is connected to the dielectric function through $n = \sqrt{\mu_r \varepsilon_r}$, but we restrict the analysis to non-magnetic materials with $\mu_r = 1$. As such, we can from Eq. (3.1.3) calculate the reflection spectrum of a Drude metal described by Eq. (3.1.2). The result is shown in Figure 3.2. In the undamped case, we observe unity reflectivity below the plasma frequency and a sharp drop thereafter known as the ultraviolet transparency of metals. Increasing the damping reduces the reflection below $\omega_p$, but it always drops more sharply as $\omega$ tends towards $\omega_p$. Note that two of the values are exaggerated as example; real values for the most commonly used metals are comparable to the red line, e.g. $\gamma = 0.002 \omega_p$ for gold and $0.003 \omega_p$ for silver [37].

The Drude model assumes a bulk material where all microscopic behaviour is contained in its two parameters. However, an electromagnetic field is not screened perfectly by the free electrons at an interface, but penetrates a finite distance into the material. This distance is known as the skin depth $\delta \propto \omega_p^{-1/2}$. Intuitively this tells us that the higher the plasma frequency, the better the electrons are at screening external fields manifested in a reduction of the skin depth. For metals, where the plasma frequency typically is very high due to the high electron density, we indeed find it on the scale of 10s of nanometres, e.g. $\sim 25\,\text{nm}$ at an energy of $1.96\,\text{eV}$ ($\lambda = 632\,\text{nm}$) for gold [38]. As such this effect can be ignored in many cases, but when structures become smaller than the skin depth, or thin films of a material are considered, the properties change compared to that of the bulk counterpart.

A shortcoming of the Drude model concerning bulk behaviour arises when comparing the Drude parameters for two of the most commonly used noble metals: Silver has $\hbar \omega_p = 9.01\,\text{eV}$ and $\hbar \gamma = 18\,\text{meV}$, while gold has $\hbar \omega_p = 9.03\,\text{eV}$ and $\hbar \gamma = 27\,\text{meV}$ [37]. These parameters are almost identical, but the appearances of
3.1. The basics of a metal

Figure 3.3: (a) Electronic band structure of gold calculated using density functional theory. The Fermi level is set to zero (dashed line). The red line indicates topmost occupied 5d-states, while the blue lines indicate lowest empty 6s-p-states. Figure from [39]. (b) Imaginary part of the dielectric function for gold. Solid triangles: experimental data. Dashed line: contribution from X-transitions. Dot-dashed line: contribution from L-transitions. Solid line: total theoretical calculation. Figure from [40].

Gold and silver are very different. Indeed, there is more going on connected to the electronic band structure, which we will take a closer look at in the following.

3.1.2 Interband transitions

To gain more insight into the optical response of a material, we have to examine the electronic band structure. An example of this is shown in Figure 3.3a calculated from density functional theory [39]. The dashed line at 0 eV indicates the Fermi level, which shows that gold indeed has an open Fermi surface. What differentiates the colour of gold from silver is the position of the interband absorption edge, where electrons from the lower-lying d-band states (red line) can be excited to the higher-lying sp-states (blue lines). Normally these optical transitions have very low probability, but the high density of states in solids increases the transition probability making them important for the optical response. We see that the lowest transition lies near the high-symmetry X-point around 2 eV (≈ 620 nm), and another one is found at the L-point around 2.4 eV (≈ 517 nm). This finding is directly reflected in the imaginary part of the dielectric function for gold, which is linked to absorption in the material, seen in Figure 3.3b. The contribution from X-transitions starts just below 2 eV, but it becomes dominated by the L-transitions above 2.4 eV. The strong response around these points is caused by a Van Hove-singularity in the density of states, with the one at the L-point exhibiting a stronger divergence and therefore also a stronger response [40].

In comparison, the interband absorption edge for copper lies at 2.2 eV giving it a more red colour than the yellow of gold, while the absorption edge for silver lies at 4 eV (≈ 310 nm) explaining the shiny, metallic appearance [7, p. 188-190].
These interband transitions can be taken into account by introducing them on a parameterised form as a sum of $N$ Lorentzian resonances (also called oscillators) in the dielectric function Eq. (3.1.2), known as the Drude-Lorentz model:

$$\varepsilon_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} + \sum_{i=1}^{N} \frac{f_i}{\omega_i^2 - \omega^2 - i\gamma_i\omega},$$  

(3.1.4)

where $f_i$ is the oscillator strength, $\omega_i$ the resonance frequency, and $\gamma_i$ the damping of the $i$th oscillator. We will use a similar expression later when modelling the dielectric function of a 2D material, where the oscillators represent excitonic resonances (see Chapter 4).

A comparison between the Drude-Lorentz model with $N = 5$ [41], the Drude model, and experimental data [42] is shown for gold in Figure 3.4. As can be seen, the Drude-Lorentz model captures the effect of the interband transitions very well, even though the model is still relatively simple. More elaborate models to describe the response have been made, e.g. by basing the response on the joint density of states [43]. The take-home message, however, is that for regions where no interband transitions take place, i.e. where the metal can be treated as a perfect conductor with little absorption, the Drude model can be used with great success.

In the next section we will take a closer look at light-matter interactions in metals and especially what happens when we start reducing the size of the metal structures.

### 3.2 Introduction to plasmons

So far we have only been considering single-electron excitations when looking at the Drude response and interband transitions in metals. However, the free electrons in a material can also oscillate in unison when coupled to an electromagnetic field. This collective oscillation is known as a plasmon. At the plasma frequency, where the electric field can penetrate the material, we find the bulk plasmon, where the

---

1 The experimental data from the paper is actually a determination of the refractive index, but we can get the reflectivity using Eq. (3.1.3).
3.2. Introduction to plasmons

Figure 3.5: Sketch of a propagating surface plasmon polariton at the interface between two semi-infinite half planes of a dielectric (upper) and a conductor (lower). The surface confinement is indicated by the exponential decay of the z-component of the electric field.

Conduction electrons inside the material take part in the oscillation. As the name implies this plasmon arises from the bulk properties and as such is difficult to manipulate. Of much more interest both for fundamental studies and applications are two other types of plasmons: The surface plasmon polariton\(^2\) (SPP), and the localised surface plasmon (LSP), both of which will be introduced in this section. From here we will venture into the concept of how small particles interact with an electromagnetic field, and finally what happens when two of these particles are brought in close vicinity.

3.2.1 Surface plasmon polaritons

To elucidate on the nature of SPPs we investigate the geometry shown in Figure 3.5: Two semi-infinite half planes separated at \(z = 0\), with a dielectric in the upper half space \((z > 0)\) of positive dielectric function \(\varepsilon_d\) (which can be energy dependent, but for simplicity we will assume it constant), and a conductor in the lower half space \((z < 0)\) with dielectric function \(\varepsilon_m(\omega)\). We are searching for propagating modes confined to the interface at \(z = 0\), i.e. with exponential decay in the \(z\)-direction as indicated in the figure. Using Maxwell’s equations we find for transverse magnetic (TM) polarisation (see e.g. Maier [44, p. 21-25]) in the upper half plane \(z > 0\)

\[
\mathcal{H}_y(z) = A_2 e^{i\beta x} e^{-k_d z}, \quad (3.2.1a)
\]

\[
\mathcal{E}_x(z) = iA_2 \frac{1}{\omega \varepsilon_0 \varepsilon_d} k_{d,z} e^{i\beta x} e^{-k_d z}, \quad (3.2.1b)
\]

\[
\mathcal{E}_z(z) = -A_2 \frac{\beta}{\omega \varepsilon_0 \varepsilon_d} k_{d,z} e^{i\beta x} e^{-k_d z}, \quad (3.2.1c)
\]

and for \(z < 0\) we have

\[
\mathcal{H}_y(z) = A_1 e^{i\beta x} e^{k_m z}, \quad (3.2.2a)
\]

\[
\mathcal{E}_x(z) = -iA_1 \frac{1}{\omega \varepsilon_0 \varepsilon_m(\omega)} k_{m,z} e^{i\beta x} e^{k_m z}, \quad (3.2.2b)
\]

\[
\mathcal{E}_z(z) = -A_1 \frac{\beta}{\omega \varepsilon_0 \varepsilon_m(\omega)} k_{m,z} e^{i\beta x} e^{k_m z}. \quad (3.2.2c)
\]

\(^2\) The term “polariton” is used when coupling a magnetic or electric dipole-carrying excitation to an electromagnetic field. As we shall see later in Chapter 6, this interaction can either be weak or strong, where an SPP belongs to the strong interaction regime between the incident electromagnetic field and the electron gas in the metal.

\[\text{}\]
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Figure 3.6: Dispersion relation for surface plasmon polaritons at an air/metal interface for both the damped (red) and undamped (blue) case. The air has $\varepsilon_d = 1$, and the metal uses the Drude model with $\gamma = 0.05 \omega_p$ in the damped case. Also shown is the light line for air (green) and glass (orange). The dashed line indicates the surface plasmon frequency in air, $\omega_{sp} = \omega_p / \sqrt{2}$.

Here, $H_i (E_i)$ is the respective component of the magnetic (electric) field, $A_i$ the magnitude of the magnetic field in the two half-planes, $\beta = k_z$ is the propagation constant, and $k_{i,z}$ is the z-component of the wavevector perpendicular to the interface. From the above equations we see we indeed have exponential decay of the fields in the z-direction with a characteristic decay length $L_i,z \propto k_i^{-1},z$. The boundary conditions require continuity of $H_y$ and $\varepsilon_i E_z$ which yields

$$\frac{k_{d,z}}{k_{m,z}} = -\frac{\varepsilon_d}{\varepsilon_m(\omega)}.$$  \hspace{1cm} (3.2.3)

Since $k_{i,z} > 0$, we see that these surface waves can only exist when $\text{Re}(\varepsilon_m(\omega)) < 0$, because we have assumed $\varepsilon_d$ positive. This is the reason why we require the lower half plane to be a conductor, as these naturally have negative real parts of the dielectric function in certain energy ranges (for a Drude metal with negligible damping this is the case for $\omega < \omega_p$). Combining Eq. (3.2.3) with momentum conservation $k_{i,z}^2 = \beta^2 - \varepsilon_i k_0^2$ yields the dispersion relation for propagating SPPs

$$\beta = k_0 \sqrt{\frac{\varepsilon_m(\omega)\varepsilon_d}{\varepsilon_m(\omega) + \varepsilon_d}}.$$  \hspace{1cm} (3.2.4)

It is important to note here that this dispersion relation is only valid for TM modes; doing similar calculations for transverse electric (TE) modes shows that no solutions exist. Plotting a rescaled form of Eq. (3.2.4) using a simple Drude model for $\varepsilon_m(\omega)$ and air in the upper half-plane results in Figure 3.6, where both the damped and undamped cases are seen. For the undamped case no solutions exist for a wide range of energies until the material becomes transparent at $\omega = \omega_p$, and as such propagation inside the metal is prohibited in this energy range. For large wavevectors the frequency approaches the surface plasmon frequency $\omega_{sp} = \omega_p / \sqrt{1 + \varepsilon_d}$ as is also indicated by the dashed line in Figure 3.6, where the group velocity tends to

$\text{Certain structures such as quantum dots [45] can also exhibit resonances strong enough to have } \text{Re}(\varepsilon) < 0 \text{ in a limited range around the resonance energy, but the broadband negative dielectric function is characteristic for conductors.}$
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zero. This means we have slower-moving modes and tighter surface confinement (since \( k_{i,z} \) depends on \( \beta \)). When losses are introduced, we see solutions for all \( \omega \) with the characteristic back-bending of the dispersion relation, with leaky modes in the region where \( \text{Im}(\beta) > 0 \). The losses therefore sets a lower limit for the attainable wavelength of the plasmon through \( \lambda_{sp} = \frac{2\pi}{\text{Re}(\beta)} \), as well as the surface confinement.

A final point is the position of the light line relative to the SPP dispersion. Since light carries little momentum, it is difficult to couple to the propagating plasmon mode with free-space light except for small \( \beta \) where the lines coincide. As such specialized techniques are needed to excite the SPPs. One way to do this is to use prism coupling, where a glass prism in close proximity to a thin metal film allows SPP excitation due to the decreased slope of the light line as shown in Figure 3.6; this is also called the Otto-Kretschmann configuration from the inventors of the technique \([46, 47]\). Another way is to use a grating in the metal film. Here, the grating assists in redistributing the momentum of the incoming light to the in-plane component, which allows for launching SPPs. This extra momentum can also come from using a scattering scanning near-field optical microscope (sSNOM), where light is focused on a probe with a small tip radius close to the sample. Light scattered off the tip will have evanescent modes with large \( k \)-vectors, which allows for local excitation of the SPPs. This technique furthermore has the advantage of providing very localised spectral information due to the small tip size \([48, 49]\).

3.2.2 Localised surface plasmons

In the previous section, we considered modes at a semi-infinite half-plane. Now, we will investigate what happens when we reduce the irradiated material to a particle of radius \( R \ll \lambda \), with \( \lambda \) being the wavelength of the incoming field. In the following, we will summarise a few key results from the analysis. For the full derivation I can highly recommend the classic work by Bohren and Huffman \([50]\).4

We investigate the geometry shown in Figure 3.7a, where we have a uniform spherical particle of radius \( R \) and dielectric function \( \epsilon_m(\omega) \) situated in a medium with dielectric function \( \epsilon_d \). The particle is irradiated with an incoming electric field \( E_0 \) with a single wavelength \( \lambda \gg R \). Because of this we can use the quasi-static approximation, meaning the electric field at any given point in time can be considered constant over the size of the particle. Using the spherical symmetry of the problem, the solution can be written in terms of Legendre polynomials. Matching the boundary conditions yields the induced dipole moment \( \mathbf{p} \), and from the definition of the polarisability of the sphere \( \mathbf{p} = \epsilon_d \alpha E_0 \) we find

\[
\alpha = 4\pi R^3 \frac{\epsilon_m(\omega) - \epsilon_d}{\epsilon_m(\omega) + 2\epsilon_d} \tag{3.2.5}
\]

4Although the mathematics and expressions are involved, the tone is light and the writing scattered with the occasional witty comment.
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Figure 3.7: (a) Sketch of a spherical particle much smaller than the wavelength of the incident electromagnetic field situated in a dielectric medium. (b) Absorption and scattering cross section of a gold sphere of radius $R = 25$ nm normalised to the geometric area. Note that $\sigma_{\text{scat}}$ has been multiplied by 10.

In order to connect this to physically measurable quantities, we introduce the absorption, scattering, and extinction cross sections defined as

\[
\sigma_{\text{abs}} = k \text{Im}(\alpha) = 4\pi x^{2} \text{Im} \left( \frac{\varepsilon_{m}(\omega) - \varepsilon_{d}}{\varepsilon_{m}(\omega) + 2\varepsilon_{d}} \right), \tag{3.2.6a}
\]

\[
\sigma_{\text{scat}} = \frac{k^{2}}{4\pi} |\alpha|^{2} = \frac{8}{3} x^{4} R^{2} \left| \frac{\varepsilon_{m}(\omega) - \varepsilon_{d}}{\varepsilon_{m}(\omega) + 2\varepsilon_{d}} \right|^{2}, \tag{3.2.6b}
\]

\[
\sigma_{\text{ext}} = \sigma_{\text{abs}} + \sigma_{\text{scat}}, \tag{3.2.6c}
\]

where we have introduced the dimensionless parameter $x = kR$. Since we have made no further assumptions about the magnitude of $R$ or $\lambda$, we can infer that as long as $x \ll 1$ the equations (3.2.6a)-(3.2.6c) are valid. We can furthermore conclude that when the polarisability diverges, the respective cross sections will as well. From this we get the Fröhlich resonance condition $\text{Re}(\varepsilon_{m}(\omega)) = -2\varepsilon_{d}$. As was the case for the SPPs, we therefore need $\text{Re}(\varepsilon_{m}(\omega)) < 0$, i.e. a conducting material. This strong dependence of the resonance energy on the surrounding medium has found applications in refractive index sensing using plasmonic structures [51, 52].

Calculated spectra for a gold sphere of radius $R = 25$ nm using the dielectric function by Rakić et al. [41] are depicted in Figure 3.7b. The peak around 2.5 eV is the LSP resonance, and it is clearly located at the onset of the interband transitions represented by the large background at higher energies. For small particles the absorption typically dominates $\sigma_{\text{ext}}$, while the blueshift between absorption and scattering is both predicted from Mie theory and observed experimentally [33].

The LSP can be understood as a standing-wave pattern on the surface of the particle as can be seen for the case of a silver nanorod in Figure 3.8a. The electron wave needs a phase shift of a multiple of $2\pi$ on a full round-trip giving dipolar, quadropolar, and higher-order modes. For gold, higher-order modes are difficult to observe due to the low-energy absorption edge, but in metals like silver they are more readily available [31, 53]. However, these higher-order modes can be difficult to excite because of the
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**Figure 3.8:** (a) Experimental (left) and simulated (right) mode profile of a silver nanorod of length 192 nm and diameter 20 nm measured using electron energy loss spectroscopy. The mode at 0.7 eV is the dipolar mode, while the one at 1.9 eV is quadropolar. Both excitations exhibit a clear standing-wave pattern. The scale bar shows the enhancement of the electric field as given by $|E_{local}|^2 / |E_0|^2$. Figure from [53]. (b) Mode evolution and extinction strength as a function of inter-particle separation for two spherical gold particles of radius $R = 25$ nm. Figure from [56].

Dipolar excitation of an incoming plane wave. This can be mitigated by using specialised techniques such as electron energy loss spectroscopy [54], as was also the case in Figure 3.8a, where the inhomogeneous field created by the electrons more readily couples to the non-dipolar modes [55]. In Figure 3.8a we furthermore see another striking feature of plasmonic resonances: the electromagnetic field enhancement. Due to the large confinement of the field, the mode energy gets concentrated in a smaller volume leading to local field enhancements in the range of 10-100 for a single particle.

Additionally, from Eq. (3.2.6a)-(3.2.6)b we see that, in the quasi-static approximation, only the strength of the resonance and not the position changes with $R$. For larger particles this approximation breaks down due to retardation effects, because the electrons no longer have time to travel the full length of the particle before the polarity changes. Larger particles typically experience a redshift and broadening of their resonance.

**Mode hybridisation**

When two particles with LSP resonances are brought in close vicinity to form a dimer, the individual modes will hybridise resulting in new resonances. The effect of this can be seen in Figure 3.8b for two spherical gold nanoparticles with radius $R = 25$ nm [56]. The lowest energy mode for positive separations is the bonding dipolar mode, where the electrons in both particles oscillate in phase. Higher-energy modes typically have more complex charge distributions, as was also the case for the silver nanorod. When the gap decreases all modes redshift until about 4 Å, where quantum mechanical effects related to the inter-electron pressure and electron tunnelling across the junction become important [56, 57]. Finally, at contact a new plasmonic mode arises called the charge transfer plasmon (CTP) associated with the physical transfer of electrons across the conductive bridge formed. In order to fully
Chapter 3. Optical Properties of Metals

capture these dynamic effects more advanced models have to be employed, e.g. the
generalised nonlocal optical response theory \([57]\), or density functional theory.
The extreme confinement of the mode in the gap between the particles also further
increases the plasmonic field enhancement. The particles in Figure 3.8b exhibit enhan-
cements as high as \(|E_{\text{local}}/E_0| = 5000\) for the smallest gaps. These extreme fields
have e.g. been used in surface enhanced Raman scattering, where laser light is used
to probe the vibrational fingerprint of molecules, to push the detection limit to the
single-molecule regime \([58]\).

3.3 Gold particles on ultra-flat surfaces

Facets terminated with the \(\{111\}\) crystal face are known to host surface states in no-
bile metals, effectively creating a 2D electron gas (2DEG) at the interface \([59, 60]\).
Studies of these states have previously involved microscopic techniques such as
scanning tunnelling microscopy (STM) to probe them due to a lack of large-scale
\(\{111\}\) facets. However, advances in the synthesis of gold flakes has allowed for the
fabrication of \(\{111\}\)-terminated, single-crystalline gold flakes on the order of 100s of
\(\mu\)m \([61]\).

As we saw in the previous section, the field intensities created when two particles
form a narrow gap can increase 1000-fold from the exciting field. This same be-
vaviour can be mimicked when placing the particle on a metallic substrate. In the
presence of an external charge distribution, the metal will mirror it to cancel out the
field created by the charges. A well-known example of this is the single point charge
over a conducting substrate, where the solution to the electric field exactly corre-
sponds to another point charge of equal magnitude but opposite sign positioned
inside the substrate. A particle on a mirror will therefore feature similar field en-
hancements with the gap formed at the interface where the surface states of the
\(\{111\}\) facet are. The hypothesis was therefore that these surface states will affect
the optical response of the system, and that this response could be used to probe the
nature of the surface states.

3.3.1 Sample preparation

In order to verify this hypothesis, two different samples were made: One with a
polycrystalline gold substrate, the other with single-crystalline (SC) gold flakes.
The polycrystalline gold mirrors were fabricated by template stripping (TS) \([62]\):
First, the gold was evaporated onto \(p\)-doped silicon substrates of very low surface
roughness following the recommendations of McPeak et al. \([63]\) to use low deposi-
tion rates (0.1 nm/s). Thereafter the gold was covered with an optical epoxy (Nor-
land Optical Adhesive 60) and a glass slide. After curing the epoxy with UV light,
the glass slide, epoxy, and gold were peeled off the silicon substrate revealing the
gold, which had conformed to the low roughness of the silicon to give an ultra-flat,
polycrystalline surface. The native oxide layer formed on the silicon surface will
impact the resulting roughness of the gold surface. Removing this oxide layer be-
fore gold deposition, however, hinders the process of template stripping, as the gold
forms a eutectic alloy with the silicon promoting a strong bonding. Indeed, gold is
commonly used as an intermediate layer to bond wafers of silicon together \([64]\).
3.3. Gold particles on ultra-flat surfaces

![Figure 3.9: (a) Example spectrum of a nanoparticle on the polycrystalline template-stripped gold. The lowest energy peak is the gap plasmon mode, but notice also the shoulder at around 1.75 eV. (b) Distribution of fitted peaks of the gap plasmon mode on template-stripped gold (top) and single-crystalline flakes (bottom).](image)

The SC gold flakes were chemically synthesised by Enno Kraus\textsuperscript{5} using a method described elsewhere \cite{61}. In short, a \ce{HAuCl4} precursor was used and treated with further chemicals to begin the seeding. Substrates were placed directly into the seed solution for a prolonged period (around 72 hours), after which the flakes could be found both on the substrate and in the solution.

Surface roughness is known to play an important role in the optical response of these narrow-gap systems since this can influence the gap size \cite{65,66}. As such the surface roughness would have to be the same between the two samples in order to compare. Atomic force microscopy (AFM) measurements showed a nearly flat surface with a root-mean square (RMS) surface roughness of the TS substrate of 200 pm, which is close to the one measured on the underlying silicon substrate of 100 pm. The SC flakes also showed an RMS surface roughness around 200 pm (for comparison the lattice constant of gold is 407.82 pm).

The spherical gold nanoparticles were bought from BBI Solutions and had a mean diameter of 80 nm with a variation ≤ 8 %. These particles are capped with a thin citrate layer in order to avoid clustering in the solution. Deposition was performed using a simple dropcast method. A small amount of the liquid (100-200 µL) was deposited on the substrate and left for 60 s, after which it was quickly blown off using a strong burst of \ce{N2} gas. Depending on the specific substrate these deposition conditions can be optimised to ensure a sparse enough coverage of particles allowing for single-particle spectroscopy.

3.3.2 Methods and results

Darkfield spectra were recorded for individual particles on the TS and SC gold. All spectra were recorded using a CFI TU Plan Fluor EPI 100x (0.9 NA) objective and an exposure time of 20 × 5 s. In total 50 and 64 particles were measured from the TS and SC gold, respectively.

\textsuperscript{5}From Prof. Bert Hecht’s group at the University of Würzburg.
A sample spectrum from the TS substrate can be seen in Figure 3.9a. The lowest energy mode is the gap plasmon \[66\], where the majority of the field energy is confined in the narrow gap around the touching point between the particle and substrate. Close to this we see a shoulder peak as well as two other peaks of higher energy. To represent this all spectra were fitted with four Voigt profiles\[6\]. The result of this fit can be seen in Figure 3.9b in the case of the gap plasmon mode for the TS substrate (top) and the SC flakes (bottom). In order to compare the two results, a normal distribution is fitted to the fitted parameters, which yields a mean value \( \mu = 1.64 \pm 0.01 \) eV and standard deviation \( \sigma = 30 \pm 5 \) meV for the TS sample, and \( \mu = 1.64 \pm 0.01 \) eV and \( \sigma = 29 \pm 4 \) meV for the SC flake.

3.3.3 Discussion and outlook

The results from the fit to the gap plasmon mode are inconclusive: No statistical significance is observed between the two different substrates. Additionally, it was later discovered that organic residues from the synthesis process may have been present on the SC flakes. If a particle lands on a region with these organic residues, the gap distance will naturally increase resulting in a blueshift of the resonance, but the presence of a higher refractive index material in the gap counteracts this by redshifting the resonance. Without knowing the specific morphology and composition of the substrate underneath each individual particle, discerning between these two effects is challenging.

Two ways to handle these residues were proposed: Either to plasma etch the flakes in an oxygen plasma to remove any contaminants on the surface, or to functionalise the surface with self-assembled monolayers of organic molecules in the form of thiols. The length of these (and thus the gap size) depends on the specific thiol, and this can be controlled with high precision \[65\]. AFM measurements showed that this functionalisation replaced the organic residues on the surface, and the layer of thiols additionally serves to smooth the surface further reducing the impact of surface roughness \[65\].

Finite-element method calculations were carried out by Christos Tserkezis\[7\] in order to predict the impact of the presence of this 2D electron gas and help with new sample designs. The result of these can be seen in Figure 3.10 for different gap distances and with a density of the electron gas \( n_{2D} = 2 \times 10^{18} \text{ m}^{-2} \) (Pitarke et al. \[67\] reports \( n_{2D} = 5 \times 10^{17} \text{ m}^{-2} \)). The electron gas was modelled as a surface current boundary condition, as has previously successfully been applied to graphene \[68\]. From the results no clear trend can be deduced. For the three largest gaps the 2D electron gas makes little difference in the optical response of the gap plasmon mode. For intermediate distances down to 1.5 Å a red-shift is observed, but this effect reverses when the gap decreases even further.

Previous results by Lumdee et al. \[66\] has also shown that significant variation between similar particles on the same metallic film can be observed due to surface roughness. The substrate used in their study was evaporated gold with an RMS surface roughness of 1.2 nm, significantly higher than the substrates used here. Nonetheless, this effect cannot be ruled out as we see a large variation in the expected response for even a change of 1 Å in the gap distance in both Figure 3.8b

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\[6\] The Voigt profile is a convolution between a Lorentzian and a Gaussian.

\[7\] At that time in the group, now at the University of Southern Denmark in SDU NanoOptics.
3.3. Gold particles on ultra-flat surfaces

![Graph showing optical response of a spherical nanoparticle on a gold substrate with and without the presence of a 2D electron gas with a density of \( n_{2D} = 2 \times 10^{18} \text{ m}^{-2} \). The legend reports the gap distance. The calculations were done by Christos Tserkezis.](image)

**Figure 3.10:** Optical response of a spherical nanoparticle on a gold substrate with (dashed) and without (solid) the presence of a 2D electron gas with a density of \( n_{2D} = 2 \times 10^{18} \text{ m}^{-2} \). The legend reports the gap distance. The calculations were done by Christos Tserkezis.

and 3.10. The volatility is likely caused by the singular nature of the contact point between a spherical particle and the underlying substrate.

This variation can be lessened by using the proposed solution of functionalising the substrate with thiols, but as the calculations show the impact of the surface states quickly diminishes with the gap distance. This decrease may be remedied by using differently shaped particles with a larger interaction area in the form of e.g. nanowires, which have been shown to give sub-picometer resolution on the gap distance between nanowire and metal substrate [69]. Careful engineering of the surface roughness and gap distance, possibly with the use of thiols or other organic molecules, are paramount to observe the changes induced by the surface states. Using near-field methods such as STM, the presence of the 2DEG could also be verified in the substrate prior to particle deposition. A study combining the microscopic properties of a sample with scattering experiments could then be performed to gauge the exact influence of the 2DEG on the optical response. A preliminary numerical study is recommended to screen potential sample geometries, however, in order to maximise the induced effect.
After the successful isolation of graphene in 2004 [1], it only took a few more years before another group of layered materials bound by weak Van der Waals-forces was exfoliated to monolayers using the Scotch tape method: The transition metal dichalcogenides (TMDCs). These are most commonly found in the combination MX$_2$, where M is the transition metal and X the chalcogen.

In principal, a TMDC can be formed between any transition metal and chalcogen, and indeed many hundreds have been found to be thermodynamically stable [2,70], but to give even a brief introduction to this vast array of materials and the research done is well beyond the scope of this work. We will instead focus our attention on the combinations that were among the first studied due to their natural occurrence as bulk crystals, namely the semiconducting TMDCs where M = W, Mo and X = S, Se, Te. Indeed, these materials have been known for decades and their bulk properties have been the subject of many studies [71–73], while e.g. MoS$_2$ is used extensively as a solid lubricant because of its low friction and high thermal stability. Due to their atomically thin nature, resistance to strain [4], and strong interaction with light [3], these semiconducting materials have been heralded a great future for use in nanoscale electronic components, flexible solar cells, and integrated optical devices.

In this chapter we will start with a general introduction to the TMDCs in terms of their atomic and electronic band structure, which will also include an overview of their chiral and excitonic properties. Following that is an introduction to the optical properties of these materials, and finally we will see how to extract the dielectric function from experimental data using the transfer-matrix method.

### 4.1 Atomic and electronic structure

The molybdenum and tungsten sulphides, selenides, and tellurides (hereafter referred to simply as TMDCs) all share the atomic structure trigonal prismatic (also known as the 2H). The TMDCs can also form in the octahedral structure (1T phase), but the 2H is the thermodynamically most stable and the one encountered in natural crystals, and we will therefore focus on this. Contrary to graphene, where each layer is a single sheet of carbon atoms, the 2H crystal structure consists of an M atom sandwiched between two sheets of X atoms, such that the X atoms are situated directly above each other as depicted in Figure 4.1a. Additional layers are added through a
4.1. Atomic and electronic structure

180° in-plane rotation with the metal atom sitting above a chalcogen atom, while the layers are bound together with Van der Waals-forces. We will later see that this orientation of the layers is hugely important for the electronic and optical properties, with recent examples from bilayer graphene exhibiting superconductivity when one layer is rotated by only a small angle [74], as well as additional electron-hole complexes appearing for Van der Waals-heterostructures [13–16].

Due to their in-plane hexagonal crystal structure, the TMDCs also have a hexagonal Brillouin zone as shown for MoS$_2$ in Figure 4.1b, where the high-symmetry points $\Gamma$ and $K$ are marked [75]. The Brillouin zone has two different, threefold degenerate valleys $K$ and $-K$. Since the constituent atoms of the TMDCs have large masses, spin-orbit coupling (SOC) plays an important role in their electronic properties and is the cause of the splitting seen between the two valence bands at the $K$-points (red and blue).

A more elaborate picture of the band structure of a different TMDC, WS$_2$, calculated using density functional theory (DFT) is shown in Figure 4.2 [76]. From Figure 4.2 we also directly see the impact of the SOC: Without it (top row), additional layers give rise to a nearly degenerate band manifold at the $K$-point with only small band separations. Including SOC (bottom row) splits the valence band with an energy difference of around 400 meV, a result which has also been corroborated experimentally [76]. In general the heavier the atoms, the larger the valence band splitting, which means that e.g. the lighter MoS$_2$ has a splitting on the order of $\sim$150 meV [9]. In addition to the band manifolds when additional layers are added, the TMDCs transform into an indirect bandgap semiconductor already from the bilayer case. This is caused by the interlayer hopping, which primarily happens between the $p$-orbitals of the chalcogen atoms [27], that leads to a splitting of the valence band maximum at the $\Gamma$-point, as well as an increased conduction band splitting situated in between the $K$- and $\Gamma$-point.

As we shall see in the following this transition to an indirect bandgap plays a vital role in the optical properties. First, however, we will take a closer look at the spin
properties associated with the SOC and the derived effects.

### 4.1.1 Chirality and the lifting of valley degeneracy

The SOC is, as the name implies, associated with the electron spin’s interaction with the orbital angular momentum of the electronic states. As such the split valence bands arising from this effect has different spin polarity as indicated by the arrows in Figure 4.1b. Furthermore, time-reversal symmetry and the lack of inversion symmetry in monolayer TMDCs require that \( E(K, \uparrow) = E(-K, \downarrow) \). This means the bands in different valleys have different spin polarities, and also that the spin and valley states of the electrons are coupled \([75]\). This link between the spin and valley degrees of freedom has led to the concept of valleytronics, where the valley can be used as an active control parameter in electronic and optoelectronic applications \([78, 79]\).

In multilayer samples the behaviour is affected by the interlayer hopping. The 180° rotation switches the \( K \)- and \(-K \)-valleys in successive layers. This requires the spin-conserving interlayer hopping to overcome the energy barrier introduced by the SOC. For the tungsten dichalcogenides and their associated large SOC, interlayer hopping is largely suppressed as the hopping element is of the order \( \sim 100 \text{ meV} \) \([76, 77]\). This results in the SOC being almost constant at the \( K \)-point as can be seen in Figure 4.2. For the lighter molybdenum dichalcogenides with weaker SOC, the hopping element is of roughly the same magnitude as the SOC, and therefore the splitting of the valence bands is modified with additional layers \([80]\).

We shall briefly revisit these chiral properties when investigating the optical properties, as incoming light with a selected chirality can be used to address the different valley states. But first we must cover another important aspect of the electronic states in the TMDCs.
4.1. Atomic and electronic structure

Figure 4.3: Left: Schematic of an exciton in a two-band model. After excitation and thermal relaxation to the bottom of the band, the electron and hole can form a complex known as an exciton with an energy state located in the bandgap. Right: Electric field lines of the electron and hole in a 3D and 2D matrix. Coulomb screening from the surrounding material is greatly reduced in the 2D case.

4.1.2 Excitons

When an electron is promoted to the conduction band from e.g. an optical excitation, the electron and hole thermalise through emission of phonons to the bottom of the conduction band and top of the valence band, respectively. Because of the attractive Coulomb interaction, a complex can form with a lower energy than the two particles alone. This is the exciton, and its energy state is positioned in the bandgap of the material as can be seen on the left side in Figure 4.3. The binding energy $E_b$ of the exciton is defined as the energy difference between the exciton state and the bandgap, i.e. $E_b = E_g - E_{ex}$. In normal bulk semiconductors such as GaAs and InP, this binding energy is on the order of 4-5 meV [7, p. 95-101]. Since the thermal energy at room temperature is $k_B T = 26 \text{ meV}$, these excitons are not stable at ambient conditions and can normally only be observed at cryogenic temperatures. The reason for this is the screening of the Coulomb interaction between the electron-hole pair from the surrounding 3D matrix. In 2D materials, however, only the in-plane field lines are screened while the remaining field penetrates the material above and below as is shown on the right in Figure 4.3. This results in binding energies of several hundreds of meV [2, 8], which means the excitons are highly stable even at room temperature. Because of their position deep in the bandgap, radiative recombination of the excitons is an efficient process as we shall see later. Additionally, charged exciton species, known as trions, have been observed experimentally with binding energies up to $\sim$60 meV [81], meaning they are significant even at room temperature [82, 83]. The charged excitons are technologically very interesting because they, as opposed to the neutral exciton, carries a net charge allowing for control through e.g. electrostatic gating.

With the excitons we also see the effect of the strong SOC in the TMDCs by the fact that two exciton species exist, one for each of the valence bands at the $K$-point. The low-energy transition from the topmost valence band is usually denoted as the $A$-exciton, while the higher-energy one is the $B$-exciton. Since these two excitations

---

1 A direct transition to the exciton state is possible without the need for thermalisation if the incident energy matches the exciton’s, but any higher energy can also lead to exciton formation.
come from different bands with opposite spin, they inherit the chirality of these states, but without special means of excitation there is no inherent spin polarity.

The excitons are also present in multilayer TMDCs at the K-point, but the new conduction band minimum between the Γ- and K-point opens for nonradiative pathways as this transition can be mediated by low-energy phonons. Since the density of states for these new pathways increases for additional layers, this causes the radiative efficiency of the TMDCs to become drastically reduced in multilayer samples [76].

4.2 Optical properties

4.2.1 Absorption

From the band diagrams shown in Figure 4.2 many things can be deduced about the optical properties of a material. Central to this concept is the joint density of states (JDOS), since this is closely connected to the imaginary part of the dielectric function and thus the absorption [84, p. 533-539]. The JDOS is given by [85]

$$\rho(\omega) = \frac{1}{4\pi^2} \int_{S(\omega)} \left| \nabla_k (E_c - E_v) \right|^2 dS,$$  

(4.2.1)

where $S(\omega)$ are cut-lines of constant energy in the band structure, and $E_{c(v)}$ is the energy of the conduction (valence) band. In general terms the higher the JDOS, the larger the absorption, and from Eq. (4.2.1) we see the JDOS is the largest when the denominator under the integral diverges. One possibility is $\nabla_k E_c = \nabla_k E_v = 0$, where we have a Van Hove-singularity (VHS). These are easily identified in the

Figure 4.4: (a) Band structure diagram of monolayer WS$_2$ calculated using a different density functional theory method than in Figure 4.2. Notice the change in the magnitude of the bandgap at the K-point. Van Hove-singularities are marked with red arrows, while band nesting is indicated with blue. (b) In-plane absorbance of WS$_2$ calculated using the Bethe-Salpeter equation (red) and random-phase approximation (blue). Also shown is the out-of-plane absorbance using the BSE (green). The dashed line indicates the quasi-particle bandgap. The data for both figures are from [2].
4.2. Optical properties

band diagrams as inflections in the band structure, and they are typically found around high-symmetry points. In Figure 4.4a we again have the band diagram of WS$_2$, but this time calculated with a different DFT method which more accurately reflects the bandgap. From this we see a VHS at 2.5 eV at the $K$-point, as well as at 3.8 eV at the $\Gamma$-point, both indicated with red arrows. Looking at the absorbance for a monolayer of WS$_2$, we see these singularities reflected in Figure 4.4b (for the moment focusing on the blue curve). Near the quasi-particle bandgap (marked by the dashed, vertical line) we see the first step-like increase in the absorbance, and again at the peak around 4 eV which is extended due to the coalescence of bands at the $\Gamma$-point.

However, we also see features in the band spectrum that are not explained, especially the increase around 3.5 eV. This is caused by band nesting [85], which happens when $|\nabla_k E_c| \approx |\nabla_k E_v| > 0$, i.e. where we have parallel bands with a non-zero slope. Closer inspection reveals exactly this situation at either side of the $\Gamma$-point with a band separation around 3.5 eV, as indicated by the blue arrows. The more complex high-energy response is more difficult to ascribe to individual bands due to the possible involvement of many deeper-lying states. But we are still missing a crucial component from this picture, namely the excitons. The excitonic effects are not directly visible in the band structure, and the blue curve in Figure 4.4b was calculated using the random-phase approximation, which does not take particle-particle interactions into account (e.g. the electron-hole attraction).

Including these through the Bethe-Salpeter equation results in the red curve where we see a dramatic change from the single-particle picture. First of all we immediately notice absorbance below the bandgap, which is associated with the $A$- and $B$-excitons again showing a splitting of $\sim 400$ meV. The peaks above the bandgap arise from even more exciton species [86], and in narrow energy ranges WS$_2$ exhibits absorbance in excess of 40% despite it being only a few atoms thick. Further evidence that the strong absorption originates from the excitons is the large change when going from in-plane to out-of-plane excitation as is evident from Figure 4.4b. Excitons have indeed found to be mostly in-plane [87], although interlayer excitons have been observed which also opens for the possibility to engineer hybrid exciton species between different materials [11–16].

4.2.2 Emission

Equipped with the knowledge of this chapter, understanding TMDC luminescence is fairly straightforward. When the electron-hole pair comprising the exciton recombine radiatively, a photon is emitted with an energy lower than the bandgap. If the excitation used was light, the process is known as photoluminescence (PL) (in contrast to e.g. electroluminescence where electrons are injected such as in a light emitting diode). PL spectra from different numbers of layers of WS$_2$ are seen in Figure 4.5a. In the monolayer we see a strong peak from the $A$-exciton at around 1.95 eV along with a weak signal at higher energy from the $B$-exciton. The spin-flip required for relaxation between the spin-split valence is a slow process and therefore enables $B$-exciton luminescence. As the number of layers increases, we see the relative strength of the two exciton peaks diminishes due to the increased number of nonradiative pathways, which also causes a large decrease in the integrated signal from the $A$-exciton as shown in Figure 4.5b. In addition, we observe the appearance of a third peak, $I$, corresponding to the indirect bandgap transition. As expected from the electronic band structure in Figure 4.2, the energy of this emission
decreases as more layers are added. Another interesting feature is the asymmetry of the A peak caused by the strong exciton-phonon coupling in the TMDCs [88], a feature which holds great promise for utilising this additional degree of freedom.

The strong exciton PL is due to the efficient radiative recombination of the electron-hole pair, with a quantum yield reported to reach 6% in WS$_2$ [89]. However, this is still relatively low compared to e.g. quantum dots, that have been pushed close to 100% for use as single-photon sources [90]. This indicates that significant non-radiative decay is still an issue in these 2D materials. However, researchers have recently reached near-unity quantum yield in MoS$_2$ using sulphur passivation [91], indicating that sulphur vacancies and other defects may be a significant contributor to the nonradiative processes. These shortcomings could potentially have even greater technological potential, however, as the defects have been shown to introduce additional luminescent states inside the bandgap [92, 93], that can even be used as single-photon emitters with narrow linewidths [94].

Since the excitons inherit the chirality of the constituent bands, it is possible to actively control the exciton species with circularly polarised light. On-resonant excitation of the A- and B-excitons in MoS$_2$ using circularly polarised light show unity emission polarisation of the same helicity [95]. These properties have furthermore led to the development of an electrically switchable chiral light source [96]. However, these effects are only observable at low temperature as intervalley scattering by phonons limits the degree of polarisation attainable at ambient conditions [79]. A way to circumvent this is to use the chiral properties of the excitons to directly couple to other structures, as has been demonstrated for spin-momentum locked surface plasmon polaritons [97], and plasmonic modes in a silver nanowire with a directional coupling efficiency as high as 90% [98].

In summary, the TMDCs feature varying bandgaps from the near-infrared and into the visible part of the electromagnetic spectrum [2]. Combined with their atomic thickness and inherent strong light-matter interaction they present very promising candidates for technological applications such as efficient light-harvesting [99], single-photon emitters for future quantum applications [94], and flexible electronics [5]. The introduction given in this chapter was brief by necessity, as the knowledge
about and the potential application of these materials rapidly increase. With the heralded existence of many more of these materials exhibiting possibly even stronger interaction with light, this truly is an exciting time for the field of nanophotonics.

### 4.3 Experimental determination of optical parameters

In order to model the response of a physical system containing 2D materials and thus validate experimental results, the relevant optical parameters have to be determined. There are many reports on the optical properties of these materials, but since they are highly sensitive to the surrounding environment, unique determination under the given experimental conditions is preferable when possible. A common choice to describe a material’s behaviour is the permittivity, which for a 2D material can be parameterised as a sum of Lorentzian oscillators, i.e.

\[
\varepsilon_{2D}(\omega) = \varepsilon_\infty + \sum_{i=1}^{N} \frac{f_i}{E_i^2 - \varepsilon^2 - i\gamma_i\varepsilon},
\]

where \(\varepsilon_\infty\) is the background contribution of the lattice, \(f_i\) are the oscillator strengths, and \(E_i\) and \(\gamma_i\) are the exciton energies and linewidths, respectively. In this picture each exciton (and possibly the higher excited states) is represented by a Lorentzian resonance. The usual way to determine the optical properties of thin films is to use ellipsometry, which can also be applied to 2D materials. The obvious advantage here is the direct output of the desired parameters. However, this requires specialized equipment and can be limited in resolution due to the geometry of the set up. Instead, reflection spectra can be obtained with micrometer precision from the sample under investigation and the response can be modelled using the transfer-matrix method to extract the desired parameters as described in the following.

#### 4.3.1 The transfer-matrix method

The main idea behind the transfer-matrix method is that electrical and magnetic fields at two different locations can be related to each other using a matrix method. There are two fundamental matrices in this formulation: one that connects the fields across an interface using the appropriate boundary conditions, and a propagation matrix to translate the fields across regions of homogeneous media. The following
derivation is based on the work by Zhan et al. [102] and Gonçalves and Peres [103, p. 35-38].

The geometry under investigation is depicted in Figure 4.6. Electromagnetic fields are incident from the left and right with amplitudes \( a_1 \) and \( b_{N+1} \) while the outgoing fields to the left and right have amplitudes \( b_1 \) and \( a_{N+1} \), respectively. The incident and outgoing waves are separated by \( N - 1 \) slabs with permittivities \( \varepsilon_i \) and widths \( d_{i,j} \), and these slabs are bounded by \( N \) interfaces with surface conductivities \( \sigma_i \).

We first restrict ourselves to dealing with only one interface at \( z = 0 \) bounded by two semi-infinite planes of permittivities \( \varepsilon_1 \) and \( \varepsilon_2 \). For \( s \)-polarisation (from the German “senkrecht” meaning orthogonal), also known as transverse electric (TE), the \( \mathcal{E} \)-field incident at an angle \( \theta \) is polarised along the \( y \)-direction and takes the form

\[
\mathcal{E}_{i,y} = \left( a_1 e^{ik_{i,x}z} + b_1 e^{-ik_{i,x}z} \right) e^{ik_{i,z}x - i\omega t}, \tag{4.3.2}
\]

where \( k_{i,x} \) and \( k_{i,z} \) is the \( x \)- and \( z \)-component of the wavevector \( k_i = \sqrt{\varepsilon_i \omega / c} \) at frequency \( \omega \), with \( c \) being the speed of light. Since the parallel components of the wavevector are continuous across the interface, \( k_{1,x} = k_{i+1,x} \), and \( k_{i,z} \) satisfies the relation

\[
k_{i,z}^2 = k_i^2 - k_{1,x}^2 = \frac{\omega^2}{c^2} \left( \varepsilon_i - \varepsilon_1 \sin^2 \theta \right). \tag{4.3.3}
\]

The \( \mathcal{H} \)-field can be determined from Maxwell’s equations and is given by

\[
\mathcal{H}_i = \frac{i}{\mu_0 \omega} \nabla \times \mathcal{E}_i. \tag{4.3.4}
\]

To match the fields across the interface, we invoke the boundary conditions for the \( \mathcal{E} \)- and \( \mathcal{H} \)-field:

\[
\begin{align*}
\mathbf{n} \times (\mathcal{E}_2 - \mathcal{E}_1) &= 0, \quad \tag{4.3.5} \\
\mathbf{n} \times (\mathcal{H}_2 - \mathcal{H}_1) &= \mathbf{J}, \quad \tag{4.3.6}
\end{align*}
\]

where \( \mathbf{n} \) is the unit normal vector, and \( \mathbf{J} \) is the surface current density from the 2D layer. Combining Eq. (4.3.2)-(4.3.6) along with Ohm’s Law \( \mathbf{J} = \sigma \mathcal{E} \), we obtain

\[
\begin{align*}
(a_1 + b_1) - (a_2 + b_2) &= 0, \quad \tag{4.3.7} \\
k_{1,z} (a_1 - b_1) - k_{2,z} (a_2 - b_2) &= \mu_0 \omega \sigma (a_1 + b_1), \quad \tag{4.3.8}
\end{align*}
\]

which directly relates the field amplitudes of the incident and outgoing waves. A similar calculation can be made for \( p \)-polarised (transverse magnetic, TM) light, where the \( \mathcal{H} \)-field is polarised along the \( y \)-direction. Expressing the amplitudes in medium 1 in terms of the amplitudes in medium 2 yields the first component in the transfer-matrix method, the transmission matrix

\[
\begin{pmatrix} a_1 \\ b_1 \end{pmatrix} = \mathbf{T}_{1\rightarrow 2,m} \begin{pmatrix} a_2 \\ b_2 \end{pmatrix},
\]

\[
\Rightarrow \mathbf{T}_{1\rightarrow j,m} = \frac{1}{2} \begin{bmatrix} 1 + \eta_m + \rho_m & 1 - \eta_m - \zeta_m \rho_m \\ 1 - \eta_m + \zeta_m \rho_m & 1 + \eta_m - \rho_m \end{bmatrix}, \tag{4.3.10}
\]

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4.3. Experimental determination of optical parameters

where \( m = (s, p) \) is the polarisation of the incident light, \( \zeta_s, \zeta_p = (-1, 1) \), and

\[
\eta_s = \frac{k_{j,z}}{k_{i,z}}, \quad \rho_s = \frac{\sigma\mu_0\omega}{k_{i,z}}, \quad (4.3.11)
\]

\[
\eta_p = \frac{\varepsilon_s k_{j,z}}{\varepsilon_p k_{i,z}}, \quad \rho_p = \frac{\sigma k_{j,z}}{\varepsilon_0\varepsilon_p\omega}. \quad (4.3.12)
\]

Since we are interested in the permittivity and not the conductivity, we recast the expressions in Eq. (4.3.11) using the relation \( \frac{\sigma}{\omega\varepsilon_0} = \frac{i\varepsilon}{2\varepsilon_0} \), where \( d_{2D} \) is the effective thickness of the 2D material [104], to obtain

\[
\eta_s = \frac{k_{j,z}}{k_{i,z}}, \quad \rho_s = \frac{i\omega^2 d_{2D}}{\varepsilon k_{i,z}} (1 - \varepsilon_{2D}), \quad (4.3.13)
\]

\[
\eta_p = \frac{\varepsilon_s k_{j,z}}{\varepsilon_p k_{i,z}}, \quad \rho_p = \frac{id_{2D}k_{j,z}}{\varepsilon_j} (1 - \varepsilon_{2D}). \quad (4.3.14)
\]

The second component of the transfer-matrix method is the propagation matrix, which simply adds a phase to the waves travelling forwards and backwards in the medium. As such it has the form

\[
P_{i \rightarrow j} = \begin{bmatrix}
e^{-ik_{i,z}d_{ij}} & 0 \\
0 & e^{ik_{i,z}d_{ij}}
\end{bmatrix}. \quad (4.3.15)
\]

In order to incorporate interfaces beyond the first, the transfer matrix \( M \) of the total system is found by successively multiplying propagation and transmission matrices in the associated order [86], i.e.

\[
\begin{pmatrix} a_1 \\ b_1 \end{pmatrix} = M \begin{pmatrix} a_{N+1} \\ b_{N+1} \end{pmatrix}, \quad M = T_{1 \rightarrow 2}P_{1 \rightarrow 2}T_{2 \rightarrow 3} \ldots T_{N \rightarrow N+1}. \quad (4.3.16)
\]

In order to connect the transfer matrix to physical observables, the Fresnel reflection and transmission coefficients of the combined system can be shown to be related to the elements of the transfer matrix by [86]

\[
r = \frac{M_{21}}{M_{11}} \quad \Rightarrow \quad R_{s,p} = |r_{s,p}|^2, \quad (4.3.17)
\]

\[
t = \frac{1}{M_{11}} \quad \Rightarrow \quad T_{s,p} = \chi_{s,p} |t_{s,p}|^2, \quad (4.3.18)
\]

where \( \chi_s = k_{N+1,z}/k_{i,z} \) and \( \chi_p = \varepsilon_1 k_{N+1,z}/\varepsilon_{N+1} k_{i,z} \).

The strength of the transfer-matrix method is now obvious: The individual transmission and propagation matrices are simple to construct while the presence of the 2D material can be switched off by setting \( \sigma = 0 \) to model different systems. As long as the incoming angle before the first interface is known, the continuity of \( k_x \) also ensures proper handling of refraction at the various interfaces via Eq. (4.3.3), while multiple internal reflections are automatically taken into account in this formulation. Furthermore, more exotic optical properties of the interface can be deduced from the reflection coefficient as is e.g. the case for the dispersion relation for graphene plasmons [103, p. 45-46]. Explicit analytic expressions might be difficult to obtain for complex geometries, but the problems can still be solved numerically by applying the transfer-matrix method.
4.3.2 Three-layer interface with a 2D material

2D materials have in previous works been exfoliated directly on a single-interface substrate which eases the theoretical modelling [86], but studies have shown that the interference created by having a multilayered substrate can increase the optical contrast of few- and even monolayer 2D materials [105]. For this reason, the 2D materials used throughout this work have all been exfoliated on a silicon substrate with a thermally grown oxide layer (typically between 90 nm and 300 nm). In the following we will apply the transfer-matrix method to this geometry depicted in Figure 4.7: WS$_2$ exfoliated on a silicon substrate with a thermally grown silicon dioxide layer constituting a three-interface system, with a surface conductivity representing the WS$_2$ at the first air/SiO$_2$-interface. We do this to model the reflectance of the system in order to determine the permittivity from experimental reflection spectra. Since the incident light used is unpolarised, we will need to consider both s- and p-polarisation. Constructing the resulting five matrices for this problem using Eq. (4.3.10) and Eq. (4.3.15) yields

$$T_{1\rightarrow2,s} = \frac{1}{2} \begin{bmatrix} 1 + \frac{k_{2z}}{k_{1z}} + i\frac{\omega^2 d_{2D}}{c^2 k_{1z}} (1 - \varepsilon_{2D}) & 1 - \frac{k_{2z}}{k_{1z}} + i\frac{\omega^2 d_{2D}}{c^2 k_{1z}} (1 - \varepsilon_{2D}) \\ 1 - \frac{k_{2z}}{k_{1z}} - i\frac{\omega^2 d_{2D}}{c^2 k_{1z}} (1 - \varepsilon_{2D}) & 1 + \frac{k_{2z}}{k_{1z}} - i\frac{\omega^2 d_{2D}}{c^2 k_{1z}} (1 - \varepsilon_{2D}) \end{bmatrix},$$  

(4.3.19)

$$T_{1\rightarrow2,p} = \frac{1}{2} \begin{bmatrix} 1 + \frac{\varepsilon_{1} k_{2z}}{\varepsilon_{2} k_{1z}} + i\frac{d_{2D} k_{2z}}{\varepsilon_{2} k_{1z}} (1 - \varepsilon_{2D}) & 1 - \frac{\varepsilon_{1} k_{2z}}{\varepsilon_{2} k_{1z}} - i\frac{d_{2D} k_{2z}}{\varepsilon_{2} k_{1z}} (1 - \varepsilon_{2D}) \\ 1 - \frac{\varepsilon_{1} k_{2z}}{\varepsilon_{2} k_{1z}} + i\frac{d_{2D} k_{2z}}{\varepsilon_{2} k_{1z}} (1 - \varepsilon_{2D}) & 1 + \frac{\varepsilon_{1} k_{2z}}{\varepsilon_{2} k_{1z}} + i\frac{d_{2D} k_{2z}}{\varepsilon_{2} k_{1z}} (1 - \varepsilon_{2D}) \end{bmatrix},$$  

(4.3.20)

$$P_{1\rightarrow2} = \begin{bmatrix} e^{-ik_{2z} d_{1z}} & 0 \\ 0 & e^{ik_{2z} d_{1z}} \end{bmatrix},$$  

(4.3.21)

$$T_{2\rightarrow3,s} = \frac{1}{2} \begin{bmatrix} 1 + \frac{k_{2z}}{k_{1z}} & 1 - \frac{k_{2z}}{k_{1z}} \\ \frac{k_{2z}}{k_{1z}} & 1 + \frac{k_{2z}}{k_{1z}} \end{bmatrix},$$  

(4.3.22)

$$T_{2\rightarrow3,p} = \frac{1}{2} \begin{bmatrix} 1 + \frac{\varepsilon_{1} k_{2z}}{\varepsilon_{2} k_{1z}} & 1 - \frac{\varepsilon_{1} k_{2z}}{\varepsilon_{2} k_{1z}} \\ \frac{\varepsilon_{1} k_{2z}}{\varepsilon_{2} k_{1z}} & 1 + \frac{\varepsilon_{1} k_{2z}}{\varepsilon_{2} k_{1z}} \end{bmatrix}.$$  

(4.3.23)
Multiplying these together using Eq. (4.3.16) gives the transfer matrix. Since we are interested in the reflection, the important elements of \( M \) are

\[
M_{11,m} = \begin{pmatrix} T_{1\to 2,m} & P_{1\to 2} \end{pmatrix}_{1,1} \begin{pmatrix} T_{2\to 3,m} \end{pmatrix}_{1,1} + \begin{pmatrix} T_{1\to 2,m} & P_{1\to 2} \end{pmatrix}_{1,2} \begin{pmatrix} T_{2\to 3,m} \end{pmatrix}_{2,1},
\]

(4.3.24)

\[
M_{21,m} = \begin{pmatrix} T_{1\to 2,m} \end{pmatrix}_{2,1} \begin{pmatrix} T_{2\to 3,m} \end{pmatrix}_{1,1} + \begin{pmatrix} T_{1\to 2,m} \end{pmatrix}_{2,2} \begin{pmatrix} P_{1\to 2} \end{pmatrix}_{2,1}. \]

(4.3.25)

The reflection coefficient is then given by

\[
r_{13,m} = \frac{\begin{pmatrix} T_{1\to 2,m} \end{pmatrix}_{2,1} \begin{pmatrix} T_{2\to 3,m} \end{pmatrix}_{1,1} e^{-ik_{2,z}d_{1,2}} + \begin{pmatrix} T_{1\to 2,m} \end{pmatrix}_{2,2} \begin{pmatrix} T_{2\to 3,m} \end{pmatrix}_{2,1} e^{ik_{2,z}d_{1,2}}}{\begin{pmatrix} T_{1\to 2,m} \end{pmatrix}_{1,1} \begin{pmatrix} T_{2\to 3,m} \end{pmatrix}_{1,1} e^{-ik_{2,z}d_{1,2}} + \begin{pmatrix} T_{1\to 2,m} \end{pmatrix}_{1,2} \begin{pmatrix} T_{2\to 3,m} \end{pmatrix}_{2,1} e^{ik_{2,z}d_{1,2}}}. \]

(4.3.26)

Since the transfer matrix for a single interface is simply the relevant transmission matrix, we have \( r_{ij,m} = \begin{pmatrix} T_{i\to j,m} \end{pmatrix}_{1,1} \begin{pmatrix} T_{1\to 2,m} \end{pmatrix}_{1,1} \). Using this we can reduce Eq. (4.3.26) to

\[
r_{13,m} = \frac{r_{12,m} + r_{23,m} \begin{pmatrix} T_{1\to 2,m} \end{pmatrix}_{2,2} e^{2ik_{2,z}d_{1,2}}}{1 + r_{23,m} \begin{pmatrix} T_{1\to 2,m} \end{pmatrix}_{1,1} e^{2ik_{2,z}d_{1,2}}}. \]

(4.3.27)

From Eq. (4.3.10) we can furthermore deduce that \( \begin{pmatrix} T_{1\to 2,m} \end{pmatrix}_{1,1} = -r_{21,m} \) which gives the final form of the reflection coefficient for the three-interface system studied here:

\[
r_{13,m} = \frac{r_{12,m} + r_{23,m} \begin{pmatrix} T_{1\to 2,m} \end{pmatrix}_{2,2} e^{2ik_{2,z}d_{1,2}}}{1 - r_{21,m} r_{23,m} e^{2ik_{2,z}d_{1,2}}}. \]

(4.3.28)

As a final note it can be added that in the absence of the 2D material, we have \( \begin{pmatrix} T_{1\to 2,m} \end{pmatrix}_{1,1} = \begin{pmatrix} T_{1\to 2,m} \end{pmatrix}_{2,2} \) and \( r_{12,m} = -r_{21,m} \) so we recover the usual expression for the reflection coefficient of a three-interface system.

**4.3.3 Fitting to experimental data**

Experimental reflection spectra were obtained from five separate monolayer WS\(_2\) flakes using the halogen lamp and a pinhole to spatially filter the incoming light and achieve close to only normal incidence of the light. The formulas above do allow for varying the angle of incidence, but given that the angular distribution of the unfiltered white light is unknown, the resulting fit would be attached with a higher degree of uncertainty.

In order to match experimental and theoretical spectra and extract the permittivity, a common normalization had to be chosen to correctly adjust the counts. In this case the bare Si/SiO\(_2\) substrate was chosen as it can readily both be simulated and measured. However, several things can impact this result: Variation in the substrate morphology can lead to differences in the SiO\(_2\) thickness, the refractive index of our sample can be different from the literature values used (Ref. [106] for Si and Ref. [107] for SiO\(_2\)), and uncertainties in the absolute value of the signal are inherent in any measurement. We therefore allow for a shift in the total signal resulting in the
Chapter 4. The Transition Metal Dichalcogenides

Figure 4.8: Example spectrum of the reflection of a monolayer WS$_2$ flake normalized with the bare Si/SiO$_2$ substrate showing clear absorption dips at the position of the A- and B-exciton.

![Spectrum Graph](image)

Table 4.1: Experimentally obtained values for the parameterised permittivity of WS$_2$. $E_3$ was fixed at 2.75 eV for the analysis, while $\varepsilon_\infty$ was bounded to the low side at a value of 1. The units are $f_i$: eV$^2$, $E_i$: eV, and $\gamma_i$: meV.

<table>
<thead>
<tr>
<th>Flake</th>
<th>$\varepsilon_\infty$</th>
<th>$f_1$</th>
<th>$E_1$</th>
<th>$\gamma_1$</th>
<th>$f_2$</th>
<th>$E_2$</th>
<th>$\gamma_2$</th>
<th>$f_3$</th>
<th>$E_3$</th>
<th>$\gamma_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.958</td>
<td>2.58</td>
<td>28.5</td>
<td>3.18</td>
<td>2.32</td>
<td>110</td>
<td>49.6</td>
<td>159</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.965</td>
<td>2.81</td>
<td>26.7</td>
<td>2.82</td>
<td>2.33</td>
<td>100</td>
<td>43.2</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.962</td>
<td>2.72</td>
<td>26.9</td>
<td>2.92</td>
<td>2.33</td>
<td>103</td>
<td>43.6</td>
<td>2.75</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.968</td>
<td>2.51</td>
<td>29.2</td>
<td>2.92</td>
<td>2.33</td>
<td>108</td>
<td>46.0</td>
<td>149</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.964</td>
<td>2.60</td>
<td>27.8</td>
<td>2.90</td>
<td>2.33</td>
<td>106</td>
<td>43.8</td>
<td>122</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>1.963</td>
<td>2.65</td>
<td>27.8</td>
<td>2.95</td>
<td>2.33</td>
<td>106</td>
<td>45.2</td>
<td>2.75</td>
<td>106</td>
<td></td>
</tr>
</tbody>
</table>

The value of the background lies consistently at around $\approx -0.13 \approx 15\%$. It should be noted, however, that this parameter is highly sensitive to the exact value of the refractive index of the substrate materials, especially the SiO$_2$ as it is here the multiple internal reflections propagate. Variations in $b$ exceeding 0.05 were observed by

expression

$$R_{fit} = \frac{1}{2} \left( |r_{13,s}|^2 + |r_{13,p}|^2 \right) + b,$$  \hspace{1cm} (4.3.29)

where $b$ is the aforementioned shift of the spectra. The permittivity is parameterised as described in Eq. (4.3.1) with $N = 3$ representing the A-exciton, the B-exciton, and the background coming from the C- and D-exciton. The energy range of the spectrum does not cover these two latter peaks, and as such separate oscillators are not needed. Since we are considering monolayer flakes $\varepsilon_\infty \approx 1 [108]$, although we allow it to vary slightly. The value $d_{WS_2} = 6.18 \text{Å}$ was used corresponding to the interlayer distance of WS$_2$ in the bulk material [71]. The SiO$_2$ thickness was taken as 97.5 nm since the wafer showed variations between 95 and 100 nm.

One of the experimental spectra along with the best fit is shown in Figure 4.8, where we see excellent agreement between experiment and theory. The procedure is repeated for all five measurements, and the resulting oscillator parameters are reported in Table 4.1. In general the values are in good agreement with low spread. The value of the background lies consistently at around $-0.13 \approx 15\%$. It should be noted, however, that this parameter is highly sensitive to the exact value of the refractive index of the substrate materials, especially the SiO$_2$ as it is here the multiple internal reflections propagate. Variations in $b$ exceeding 0.05 were observed by
4.3. Experimental determination of optical parameters

![Figure 4.9: Extracted dielectric function for (a) a single layer and (b) 7 layers of WS\textsubscript{2}.](image)

Table 4.2: Experimentally obtained values for the parameterised permittivity of 7-layer WS\textsubscript{2}. \(E_3\) was fixed at 2.75 eV for the analysis, while \(\varepsilon_\infty\) was bounded to the low side at a value of 1. The units are \(f_i:\) eV\(^2\), \(E_i:\) eV, and \(\Gamma_i:\) meV.

<table>
<thead>
<tr>
<th>Flake</th>
<th>(\varepsilon_\infty)</th>
<th>(f_1)</th>
<th>(E_1)</th>
<th>(\Gamma_1)</th>
<th>(f_2)</th>
<th>(E_2)</th>
<th>(\Gamma_2)</th>
<th>(f_3)</th>
<th>(E_3)</th>
<th>(\Gamma_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1.60</td>
<td>1.942</td>
<td>44.3</td>
<td>1.49</td>
<td>2.34</td>
<td>111</td>
<td>61.1</td>
<td>2.75</td>
<td>105</td>
</tr>
</tbody>
</table>

simply using a different set of refractive index data for the SiO\textsubscript{2}. As such no further significance is ascribed to introduced correction since we note the values obtained are in good agreement with those previously reported [86].

Using Eq. (4.3.1) we can now reconstruct the dielectric function as seen in Figure 4.9a. The large, narrow response associated with the \(A\)-exciton at 1.963 eV is a testament to the strong optical response of the TMDCs as seen earlier. We furthermore note that the shape and relative magnitude of the peaks are also in good agreement with previous results [86].

Since we have only assumed that the presence of the 2D material can be represented by a boundary surface current, the transfer-matrix method has very general applicability. As an example we perform the same fitting procedure for 7-layer WS\textsubscript{2}, where now \(d_{WS_2} = 4.33\text{ nm}\). The resulting parameters can be seen in Table 4.2 with the extracted dielectric function shown in Figure 4.9b; the redshift of the \(A\)-exciton was predicted by the theory earlier in this chapter, while the broadening has also been observed in other experiments [109]. This ease of changing the system exemplifies the strength of the transfer-matrix method and its general application.
As we have seen, the TMDCs cover different spectral ranges in the visible and near-infrared, so often simply choosing the right material for the job is sufficient. Sometimes, however, additional control of the optical properties is required to e.g. resonance match with an optical cavity. This is achieved through the concept of bandgap engineering, where the band structure itself is modified [17]. For the 2D materials this technique is even more accessible due to their sensitivity to the physical surroundings. This is exemplified in the case of MoS$_2$, where the encapsulation in hexagonal boron nitride (hBN) reduced the emission linewidth by protecting the TMDC from the environment [110]. The changing band structure naturally also impacts the electronic properties, and this can be used to make spatially well-defined $p$-$n$ junctions without the need for doping as is done in traditional semiconductors [111].

In this chapter, we will explore the impact on the emission properties of encapsulating WSe$_2$ in hBN flakes, where the bottom flake is nanostructured with an antidot lattice. The initial hypothesis was that the emission will change with the hole fill fraction (HFF), which is the amount of removed hBN, in the form of the antidots, relative to the remaining.

5.1 Sample fabrication

Two samples, referenced to as 2604 and 3205, were fabricated after the same recipe by Lene Gammelgaard and Bjarke Jessen. First, a thick mechanically exfoliated hBN flake was patterned in $2 \times 2 \mu m^2$ regions defined using electron beam lithography (EBL), following the same recipe which has recently been used to open a bandgap in graphene by making antidot lattices [112]. These regions are arranged in a rectangular grid to allow for different doses of the electron beam and varying pitch (25 nm to 50 nm) of the holes. As a dose test was performed to optimise the structures, the dose number itself does not have a specific meaning, but in general the higher the dose number, the longer the electron exposure. This in turn determines the size of

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1 Both postdocs in the NanoCarbon group headed by Prof. Peter Bøggild, DTU Physics.
5.1. Sample fabrication

**Figure 5.1:** Scanning electron microscope image of the hexagonal hole grid in the bottom layer of hBN. The pitch here is 40 nm, while the dose used was 3. The scale bar is 200 nm.

**Figure 5.2:** Cross-sectional view of the two samples. The WSe$_2$ is sandwiched between two flakes of hBN, with the respective sizes indicated on the flakes. The thickness of the WSe$_2$ layer is taken as the interlayer distance in the bulk crystal [71].

the holes after etching, which have a radius on the order of 25 nm. An example scanning electron microscope (SEM) image of the resulting hexagonal grid is shown in Figure 5.1 for the case of 40 nm pitch and dose 3 (d03-p40).

After development and etching, monolayer WSe$_2$ flakes, likewise exfoliated, were picked up with a second thick hBN flake and placed on top of the structured hBN using the hot pick-up method [113]. In short, this fabrication technique utilises a polymer, which changes its adhesion with temperature. By bringing the polymer into contact with a flake and heating it past the glass transition, whereby the adhesion is increased, the flake can be picked up, and this process can be repeated to create Van der Waals-stacks of different materials. When dropping down the final stack, the polymer is cooled below the glass transition thus releasing the stack. In order to protect the more sensitive TMDCs from polymer residues and subsequent removal of these, an hBN flake can be used to pick up other flakes, as was also done here. This is viable because the Van der Waals-forces between hBN and TMDC is stronger than the adhesion to the substrate. This technique also serves to encapsulate the active material and protect it during experiments and in the long term.

A cross-sectional view of the samples can be seen in Figure 5.2, where the thickness of the hBN flakes measured using atomic force microscopy (AFM) is also indicated. Optical images of the final samples can be seen in Figure 5.3 (sample 2604) and Figure 5.4 (sample 3205). The variation in the dose is along the horizontal axis, while
Chapter 5. Bandgap Engineering of WSe₂ using Nanostructured hBN

The sample 2604. The dashed lines indicate the presence of the monolayer WSe₂ flakes, where the darker region in the leftmost flake is a bilayer. The orange circular regions on the WSe₂ are air bubbles trapped during fabrication. The hole pitch is in nm, while the dose strength is unitless.

the pitch is varied along the vertical. The spots visible on the sample predominantly over the WSe₂ flakes are air bubbles trapped during fabrication. AFM measurements confirm these areas are raised from the surrounding hBN by \( \sim 10 \text{ nm} \), meaning the WSe₂ underneath can not be considered fully encapsulated. The same is the case for the low pitch/high dose regions on the samples (e.g. top left in Figure 5.4; the colour of the structured regions is the same as the surrounding substrate). These areas have been overexposed due to the high dose and close proximity of the holes, resulting in an excessive degree of hBN etching.

5.2 Experimental results

5.2.1 Determination of the hole fill fraction

In order to test the initial hypothesis of the HFF being the important parameter, this first had to be determined. To this end, SEM images were taken of each of the 40 regions from which a measurement was obtained. However, imaging through the top hBN layer proved difficult, but since EBL is a deterministic fabrication process, regions with the same parameters were taken to be representative of each other; any microscopic variations in the individual holes are expected to be averaged out due to the large number of holes present. The uncovered part on sample 3205 had many exposed regions, and with this assumption, the SEM images could be obtained here. A representative subsection of the image was then selected to ensure uniformity and remove the influence of possible contaminants. Figure 5.1 shows an example of such a cropped image, which was used as example in the following.

In order to remove bias in the analysis, two different statistical methods were used to determine the HFF. The first one was the Gaussian Mixture Model (GMM), where a number \( N \) of normal distributions are fitted to determine subdistributions within a given overall distribution. This means the probability \( P \) of finding a pixel value \( x \)
5.2. Experimental results

Figure 5.4: The sample 3205. Two dose tests were made inverted around the dashed black line. The red dashed line indicates the position of the WSe$_2$ monolayer flake, and the circular regions of darker contrast are air bubbles trapped during fabrication. The blue part of the hBN are the unencapsulated regions. The hole pitch is in nm, while the dose strength is unitless.
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Figure 5.5: (a) Histogram of the grey-scale pixel values of Figure 5.1 with the fitted two-component Gaussian Mixture Model. (b) Resulting logical mask using the average of the two means \( \mu_1 \) and \( \mu_2 \) as the separation.

is given by

\[
P(x) = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{\sqrt{2\pi}\sigma_i} \exp\left(-\frac{(x-\mu_i)^2}{2\sigma_i^2}\right),
\]

where \( \mu_i \) and \( \sigma_i \) are the mean and standard deviation of the \( i \)th subdistribution, respectively. This choice of model was made since we expected the data histogram of the grey-scale pixel values to show a low-value peak (the holes) and a high-value one (the rest), which consequently determined the number of used subdistributions as \( N = 2 \).

The resulting fit to the distribution of grey-scale values can be seen in Figure 5.5a with \( \mu_1 = 123, \sigma_1 = 40, \mu_2 = 183, \) and \( \sigma_2 = 11 \). The high-value peak is clearly visible, but the low-value peak is not well represented by a normal distribution due to the plateau of almost equal probabilities around the pixel value 80. This means the lower distribution has a tendency to over-estimate the mean value \( \mu_1 \), a tendency that is seen throughout the fits to the histograms of the different SEM images.

To determine the HFF, the distributions were converted into a logical threshold value by taking the average of the two means \( \mu_1 \) and \( \mu_2 \). All values below this average are identified as a hole, while values above represent the unstructured part of the hBN. The result is shown in Figure 5.5b. If we compare this with the original image in Figure 5.1, we see the GMM has a tendency of over-estimating the size of the holes, which in turn is caused by the over-estimation of \( \mu_1 \). Different methods to determine the logical threshold value could be employed, but since this will only patch the symptoms and not solve the underlying problem of the fit, another method was tried as well.

This method was \( k \)-means clustering, the algorithm for which was proposed by Stuart Lloyd in 1957, although the results were not published outside the Bell Labs before 1982 [114]. The goal of \( k \)-means clustering is to partition the \( n \) observables into \( k \) clusters, such that each observable belongs to the cluster with the closest centroid giving the greatest possible distinction. Mathematically, the algorithm seeks to
5.2. Experimental results

Figure 5.6: (a) Histogram of the grey-scale pixel values of Figure 5.1 coloured according to cluster number using \( k \)-means clustering. The dashed line indicates the centroid positions. (b) The logical mask found by assignment of the two clusters.

minimise the objective function

\[
J = \sum_{i=1}^{k} \sum_{j=1}^{n} || x_j - c_i ||^2,
\]

where \( x_j \) is the position of the \( j \)th observable, \( c_i \) is the position of the \( i \)th centroid, and \( ||(\ldots)|| \) denotes the distance function, where we here used the squared Euclidean distance. As before we set the number of centroids to \( k = 2 \).

The result of the \( k \)-means algorithm can be seen in Figure 5.6a, where points belonging to the two centroids have been coloured differently. The corresponding logical mask is shown in Figure 5.6b. The centroid positions are found to be at \( c_1 = 96 \) and \( c_2 = 179 \), where we immediately see the first centroid has a lower "mean" than in the GMM. This is also reflected when comparing the logical mask. Here, we see that each individual hole in general is smaller, which is more in accordance with the SEM image in Figure 5.1. The resulting HFFs, which is found by simply counting the pixels in the mask, are in the two cases \( \text{HFF}_{\text{GMM}} = 28.3 \% \) and \( \text{HFF}_{k} = 24.0 \% \).

Due to the closer agreement of the logical mask with the SEM images found by using \( k \)-means clustering, a conclusion that is consistent with all the images, the results presented in the following have been obtained using this method.

5.2.2 Emission dependence on hole density

In order to determine the influence of the HFF on the emission properties of the WSe\(_2\), photoluminescence (PL) spectra were recorded from each individual region of structured hBN. Discarding the regions where air pockets have formed, 18 spectra from flakes on sample 2604 were obtained, and 22 spectra from 3205. The slit width was set to 250 \( \mu m \) to include only a single region without the surrounding WSe\(_2\), while the resulting signal was only taken from the pixels on the CCD corresponding to the position of the structured region. This ensures that the emission would come mostly from the structured region, while unwanted contributions to the signal are minimised. All spectra were obtained using a CFI TU Plan Fluor EPI 100x (0.9 NA)
Chapter 5. Bandgap Engineering of WSe$_2$ using Nanostructured hBN

Figure 5.7: Photoluminescence spectrum of WSe$_2$ fully encapsulated in hBN from sample 2604 (blue) with a two-peak fit (yellow; the individual peaks are shown in red and green).

objective and the 407 nm laser with an excitation power of $\sim 5$ $\mu$W and exposure time of $10 \times 1$ s.

An example PL spectrum showing the A-exciton can be seen in Figure 5.7 from fully encapsulated WSe$_2$, i.e. obtained from the space in between the structured regions. The asymmetry in the lineshape towards the lower energy side is mainly caused by the strong electron-phonon interaction in the TMDCs [88], but could also indicate the presence of the trion [115]. An ideal two-level system would result in a Lorentzian lineshape, but since the excitons are highly exposed to their surroundings from the 2D nature of the WSe$_2$, we can not expect an ideal situation. To take these considerations into account, we fit a double Voigt profile. The asymmetry in the lineshape is furthermore not captured well in a single-peak fit, and since we are interested in the position of the emission peak, we can more confidently obtain this value by using a double-peak fit. The resulting fit is plotted with the spectrum in Figure 5.7, where we indeed do see good agreement.

Several spectra from the fully encapsulated WSe$_2$ were taken as a reference in order to gauge the effect of structuring the bottom hBN layer. However, the emission energy can also vary due to changes in the local environment in the form of e.g. strain, contaminants and defects [116]. This can also lead to a shift between different flakes depending on the specific conditions during fabrication. We will therefore separate the results from 2604 and 3205, but we will assume that the three flakes in 2604 have been influenced in a similar manner by the fabrication and can therefore be analysed as a whole.

The extracted peak positions were binned together to reduce the statistical variations. The result of this procedure can be seen in Figure 5.8a-b for sample 2604 and 3205, respectively. The horizontal error bars indicate the bin width, while the vertical error bars represent the pooled uncertainty from all the measurement points from one sample. This choice was made as the variations within each bin is assumed to be of the same magnitude on the same flake (and bins with only one point would produce no error bars otherwise).

For sample 2604 there appears to be a general tendency of an increase in emission energy for larger HFFs, but the spread is significant which could be due to the assumption that the three flakes can be analysed together. The trend is somewhat
5.2. Experimental results

Figure 5.8: Peak emission energy as a function of the hole fill fraction for samples (a) 2604 and (b) 3205. The measurement points have been merged in bins of width 0.05, with the point farthest to the left corresponding to fully encapsulated WSe$_2$.

clearer for sample 3205, where we again see a general increase in the emission energy for larger HFFs. In both cases the increase is small, however, and only around $\sim$1%.

In order to analyse this further, we must understand how a larger HFF impacts the excitons. An important thing to keep in mind is that the higher the HFF, the smaller the total amount of hBN, and therefore less dielectric material is surrounding the WSe$_2$. The first interpretation of encapsulating WSe$_2$ with a dielectric would be that the exciton binding energy would decrease caused by increased screening of the electron-hole Coulomb attraction (as is e.g. the case in traditional semiconductors, where the excitons have low binding energies [7, p. 95-101]). This would cause the exciton state to move closer to the conduction band, which should result in a higher emission energy with decreasing HFF (increasing screening), which is the opposite of what we observe in Figure 5.8. According to the simple hydrogen model for excitons in semiconductors, the binding energy $E_b$ is given by [8]

$$E_b^{(n)} = \frac{\mu e^4}{2\hbar^2 \varepsilon^2 (n - 1/2)^2},$$  \hspace{1cm} (5.2.3)

where $\mu = 1/(m_e^{-1} + m_h^{-1})$ is the reduced exciton mass, $e$ is the elementary charge, $\hbar$ is the reduced Planck constant, $\varepsilon$ is the dielectric function of the environment, and $n$ denotes the order of the exciton. Although this model has been shown to underestimate the energy of the low-order excitons in the TMDCs, because of the large discrepancy between the permittivity inside the TMDC and the surroundings [8], we can still use it to a first approximation to estimate the expected change in the binding energy from a different dielectric environment. First-principle calculations for the dielectric constant of hBN at optical frequencies indicate these are $\varepsilon_\parallel = 4.97$ in-plane and $\varepsilon_\perp = 2.89$ out-of-plane [117]. In a simple model, the effective dielectric constant of the surroundings can be approximated as the average of the values above and below. From this we get a predicted change in $E_b^{(1)}$ of $\sim$150% when going from the fully to the half-encapsulated case, i.e. an increase in the exciton energy with increasing screening. In addition to the opposite direction of the shift, this is also much larger than the $\sim$1% change observed in Figure 5.8.
Besides the shortcomings in the hydrogen model, another, and well-documented, reason for this discrepancy is known as bandgap renormalisation \[17,111\]. The electrons feel the increased screening from the surroundings the same as the excitons, which limits the electron-electron Coulomb interaction and reduces the size of the bandgap. This reduction counteracts the decreased binding energy of the excitons, leaving the optical bandgap (i.e. the energy difference between the top of the valence band and the exciton energy) relatively unchanged.

In the work by Ugeda et al. \[17\] they investigated MoSe\(_2\) on both bilayer graphene (BLG) and highly oriented pyrolytic graphite (HOPG), where the HOPG screens the MoSe\(_2\) more than the BLG from the increased amount of layers. They indeed observed an exciton binding energy decrease of 51% on HOPG compared to BLG. However, the MoSe\(_2\) bandgap was reduced by 11% from BLG to HOPG due to bandgap renormalisation as well, which resulted in an increase of the optical bandgap by only 2% with the additional screening. This result is more in accordance with what we observe for our sandwiched WSe\(_2\), although the shift is still opposite to what we observe.

Another study investigating graphene-capped WS\(_2\) in reflection spectroscopy reported a redshift of the resonance for increased dielectric screening \[111\], as we also observe here. This seems to indicate that the specific effects from bandgap engineering is highly dependent on the material in question, since we see similar effects for tungsten chalcogenides, but a shift in the opposite direction for molybdenum.

Furthermore, a rapid saturation with the number of graphene capping layers was observed (within \(~5\) layers) \[111\]. As such we can safely disregard the change in bottom hBN thickness between the two samples, where both 105 nm and 32 nm are well above the saturation limit; the interlayer distance in hBN is around 0.33 nm, the same as graphene \[118\].

Another fact that could influence the spectra is the likely mixture of the two emission signals from the fully encapsulated and half-encapsulated WSe\(_2\). Since the exciton radius in TMDCs is generally on the order of a few nanometres \[119\], the exciton could be excited and recombine in either of the two regions. The change in bandgap induced by the varying dielectric environment can also function as exciton traps \[18,111\], and since the excitons can diffuse after excitation, there could be a preferred spatial recombination site. However, more investigations would be needed to estimate this effect in the current system. Separating the effects in the current measurements can not be done reliably, since the energy variation observed in Figure 5.8 is much lower than the width of the emission peak in Figure 5.7, and the strong electron-phonon coupling manifested as the low-energy tail complicates the analysis further.

### 5.2.3 Reflection spectroscopy

Calculations show that especially the higher-order excitons can be trapped by the potential well created by a changing dielectric environment \[18\], while experiments have shown the possibility to probe these higher-order excitons at low temperatures using reflection spectroscopy \[8\]. As we argued in the previous section, it was difficult to disentangle the possible contributions from the two areas of WSe\(_2\) (fully and half-encapsulated) in the PL spectra. As such reflection measurements were also
5.2. Experimental results

Figure 5.9: (a) Reflection spectra of fully encapsulated WSe$_2$ and two selected regions (dose 13 and 14, pitch 25 nm) from sample 2604. (b) Four spectra normalised to the response of the fully encapsulated WSe$_2$. The dashed line indicates the energy of the exciton.

performed on the structured regions, albeit at room temperature. The spatial region was selected in the same manner as the PL measurements, but the illumination source used here was the halogen lamp with an exposure time of $10 \times 0.1$ s.

The resulting spectra for two selected regions from sample 2604 can be seen in Figure 5.9a along with the response of the fully encapsulated WSe$_2$. All spectra are dominated by the large dip centred at 1.8 eV. Since hBN is a wide bandgap insulator, this dip is most probably caused by Fabry-Perot resonances (FPRs) in the dielectric cavity formed by the hBN, which would explain the teal colour of the hBN. This effect has also been observed in the TMDCs [120]. This assignment to FPRs also explains the varying colours on the different thicknesses of the hBN. We furthermore see a clear difference in the material response around 1.4 eV. This feature is far away from the exciton energy (indicated by the dashed line), and as such it could be an FPR in the unstructured hBN, where the presence of the holes could disrupt the resonance in the structured regions.

Curiously, around the $A$-exciton energy, no discernible change can be seen. To further elaborate on this, the same two spectra with two additional are shown in Figure 5.9b, but now normalised to the response of the fully encapsulated WSe$_2$ such that a value of 1 corresponds to an identical response between the two. A weak dip in the spectrum at the $A$-exciton energy can be observed in the green curve, although the variations in the other parts are much more pronounced. Similar variations can be observed for all the obtained spectra (not shown here) with no clear trend.

5.2.4 Discussion and outlook

One challenge in the interpretation of these reflection spectra is the unknown influence of the structured hBN, which is expected to be strong from the clear contrast differences in Figure 5.3-5.4. The $A$-exciton in WSe$_2$ is located just at the edge of the visible regime at $\sim 1.63$ eV ($\approx 760$ nm), and these two different contributions are therefore superimposed, as we also saw in Figure 5.9. Because no two nanostructured regions are the same, no reference measurement can be made to remove the varying influence of the hBN antidot lattice and isolate the response of the WSe$_2$. 
Calculations of the absorption of a WSe$_2$ monolayer can be seen in Figure 5.10 as a function of the hole radius, where only the region of the WSe$_2$ directly located over the hole is included in the calculation. For small radii, we see only a single peak of the absorption spectrum, although the spectral position is strongly dependent on the radius. For larger radii, additional peaks appear in the absorption spectrum, although they are significantly weaker than the main peak (note the logarithmic scale). These additional peaks are caused by centre-of-mass quantisation, which is caused by the confinement of the exciton momentum in the small holes [121, 122]. As for the particle-in-a-box, these energy levels move closer as the size of the confining region is increased. One important thing to note is that the additional absorption features present are not the higher-order modes of the free exciton (i.e. the 2s, 3s, etc. [8]), but is a unique consequence of the exciton confinement.

The hole radii used in these calculations are somewhat smaller than the corresponding ones in this work. However, in the time since the samples used here were fabricated, the EBL technique has been refined and resulted in the pioneering work of opening a bandgap in graphene using antidot lattices [112]. Through this refinement the smallest hole sizes achievable has been reduced to 20 nm, i.e. a radius down to 10 nm. Changing the substrate to be structured to one with a higher dielectric constant (for instance silicon), the centre-of-mass quantisation should be more pronounced and could possibly be observed at larger radii than indicated in Figure 5.10.

A new generation of samples could remedy the challenge of proper isolation of the WSe$_2$ contribution to the optical response, and possibly allow for the exploration of centre-of-mass quantisation of the excitons as well. Choosing silicon as the substrate, all regions could be fabricated and characterised using SEM before transferring the WSe$_2$/hBN stack. These regions should ideally have as small pitch and holes as possible to maximise the portion of the optical response originating from the half-encapsulated WSe$_2$. Additionally, making duplicates of the individual regions could allow for better reference measurements. If each duplicated region is both covered with the hBN/WSe$_2$ stack, as well as the hBN alone, the influence of the WSe$_2$ could more readily be isolated. Finally, the hBN flakes used here were very thick facilitating internal FPRs. Reducing the thickness would push the FPRs to higher energies,
which could make the interpretation of the spectra simpler.

More work is clearly still needed in characterising these systems, where the properties of the active material (here a TMDC) is manipulated by structuring the dielectric surroundings. The dependence of the shift direction on the encapsulated specific material hinted at by these and previous results [17, 111] is certainly interesting to pursue. This shows that although the TMDCs appear similar at first glance, once the physics are unfolded many new and unexpected differences appear.

In any case, using bandgap engineering holds great promise for tailoring the optical properties of the TMDCs. The possibility to use top-down fabrication techniques, and thereby change the optical properties of a single material in the Van der Waals stack, can have significant advantages compared with a multi-material approach. The structured dielectric surroundings could potentially also be used to create exciton traps to increase the spatial selectivity of the optical response. Finally, the possibility of exploring the fundamental excitonic properties of these two-dimensional materials in the form centre-of-mass quantisation is interesting in its own right apart from the applications.
The ability to engineer light-matter interaction lies at the heart of modern nanophotonics. Here, the coupling strength of the constituent elements is a key parameter in determining the system response. These elements can e.g. be quantum emitters in the form of excitons in either quantum dots or TMDCs, localized surface plasmons in metallic particles, dielectric cavity modes, or optical phonons. In this regard, two distinct regimes appear with very different optical responses: The weak- and the strong-coupling regime. Although strong coupling sounds more desirable at first, the weak-coupling regime is crucial in many real-world applications in, for instance, single-photon sources with high fidelity [24], lasers, photovoltaics, and surface enhanced Raman scattering [23]. In contrast, the strong coupling of light and matter has yet to find commercial success, but the field holds great promise for use in e.g. low-threshold lasers, quantum information processing, and all-optical devices [23].

In this chapter, we will start with a brief overview of the different coupling regimes and what influences the transition between them. After this, we will embark on a more in-depth description of the two. In the case of weak coupling, results will also be presented on the endeavours into coupling MoS$_2$ with gold percolation films. These semi-continuous metallic structures feature a broad range of different plasmonic excitations, as we have shown in Paper A. Furthermore, as we expand on the strong-coupling regime, the main results from Paper B will be presented along with additional details and considerations.

### 6.1 Introduction

As mentioned the coupled systems can come in any number of forms, but to ease the interpretation we will in the following restrict ourselves to the case of a cavity and an emitter represented by a two-level system. We make no assumptions to the nature of either of them at this point. They are both characterised by an energy and a linewidth, $E_{\text{cav,em}}$ and $\Gamma_{\text{cav,em}}$, for the cavity and emitter, respectively. The emitter
6.1. Introduction

Figure 6.1: Illustration of the weak- and strong-coupling regimes between a cavity and a two-level emitter. (a) Weak coupling resulting in enhanced spontaneous decay and associated photon emission. The resulting spectrum remains mostly unchanged from the interaction with the cavity. (b) Strong coupling leads to Rabi oscillations with the rate $\Omega_{\text{Rabi}}$, where energy is coherently exchanged between the cavity and emitter states. The spectrum is strongly modified from the interaction resulting in two peaks separated by an energy $E_{\text{Rabi}} = \hbar \Omega_{\text{Rabi}}$.

is positioned inside the cavity, and the joint system response to external electromagnetic fields is governed by the coupling strength $[109, 119]$

$$g = \mu \sqrt{\frac{N E_{\text{em}}}{2 \varepsilon_0 \varepsilon_r V}},$$  

(6.1.1)

where $\mu$ is the transition dipole moment of the emitter, $N$ is the number of emitters coherently participating in the coupling, $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the relative permittivity in the cavity, and $V$ is the cavity mode volume. The stronger the coupling strength, the stronger the interaction between the cavity and emitter states.

If $g$ is smaller than the intrinsic linewidths of the cavity and emitter, the coupled system is in the weak-coupling regime. Here, the emitter feels the increase in local density of states (LDOS) supported by the cavity, which leads to spontaneous emission with an altered rate compared to the vacuum as indicated in Figure 6.1a. Cavity enhancement of the radiative decay rate is known as the Purcell effect $[21]$, which can be used to control the radiative properties as well as increasing light extraction and directionality of the emitter $[22, 123, 124]$, although the emitter spectrum remains mostly unchanged.

However, when $g$ becomes larger than the energy dissipation in the coupled system, it enters the strong-coupling regime. Here, the emitter and cavity states hybridise and cease to be wholly one or the other, but are instead replaced by two dressed states. Energy is coherently exchanged between these states with a rate $\Omega_{\text{Rabi}}$ and this energy exchange is manifested in Rabi oscillations as shown in Figure 6.1b. When the cavity and emitter are perfectly resonance matched, i.e. $E_{\text{cav}} = E_{\text{em}}$, these
hybrid states are characterised by an energy splitting $E_{\text{Rabi}} = \hbar \Omega_{\text{Rabi}}$. Mode splitting is a well-known phenomenon from these coupled systems, and they can take as diverse forms as macroscopic masses coupled with springs, to two hydrogen atoms joining to form bonding and anti-bonding orbitals. In order to clearly resolve this splitting in experiments, we must require that the energy splitting is larger than the average full widths at half maximum of the coupled system constituents, i.e. that

$$E_{\text{Rabi}} > \Gamma_{\text{avg}} = \frac{1}{2} \left( \Gamma_{\text{cav}} + \Gamma_{\text{em}} \right),$$

(6.1.2)

which also serves as the criterion for entering the strong-coupling regime [109, 125, 126]. If the condition in Eq. (6.1.2) is not strictly fulfilled, spectral features can still appear that resemble strong coupling, as we shall see in the following. Careful analysis of the system response is therefore required in order to confidently identify the coupling regime.

### 6.2 Weak coupling

Far in the weak-coupling regime, the exchange rate of energy between the cavity and emitter is greatly surpassed by the dephasing processes of the system. This results in a slight shift of the complex eigenenergy of the emitter as $E_{\text{em}}' = E_{\text{em}} - i\Gamma_{\text{em}} + \Delta E_{\text{em}}$ [127]. The imaginary part of $\Delta E_{\text{em}}$ is responsible for the Purcell effect mentioned above, while the real part of $\Delta E_{\text{em}}$ is the radiative correction which shifts the emission energy of the emitter analogous to the Lamb shift [127]. This could e.g. be the case for a quantum dot positioned in a photonic crystal cavity or between two metal mirrors if the coupling strength is sufficiently small.

The manifestations of the weak-coupling regime changes depending on the magnitude of the coupling strength compared to the cavity and emitter linewidths. Since the values can change continuously, so can the nature of the interaction. Antosiewicz et al. [128] investigated this evolution for the case of a silver nanoparticle coated with a dye containing excitonic transitions, a so-called core-shell structure. By varying the size of the particle while keeping the transition dipole moment of the dye excitons constant, they could change the damping of the cavity resonance and observe different regimes. The calculated scattering and absorption spectra can be seen in Figure 6.2 on the left and right, respectively.

In Figure 6.2a-b we observe enhanced absorption, where the high damping of the particle places the system far in the weak-coupling regime. Although a splitting is observed in the scattering and extinction spectra of the coupled system, a separate identification of the contributions reveals that this dip is caused by absorption in the dye material. The excited plasmon and resulting field enhancement mediates the transfer of energy, which is subsequently absorbed in the shell. Although absorption losses are still present in the metallic core, this is outweighed by the on-resonant losses in the dye, which are ultimately responsible for the dip in scattering.

Turning to Figure 6.2c-d, we are in an intermediate regime known as induced transparency. Here, the dip in scattering and extinction is more pronounced. The metal core absorption also exhibits a stronger dip, although the absorption in the dye coating is still dominating at resonance. This leads to an overall lower scattering cross section at resonance responsible for the induced transparency. The absorption only shows weak evidence of a peak splitting, because the system is not in the strong-coupling regime and the excitons and plasmon mode are still separate excitations.
6.2. Weak coupling

Figure 6.2: Scattering and extinction (left column) and absorption (right column) of a core-shell structure indicated in the top-right corner. The subscript denotes the cross section, while the superscript indicates the simulated geometry as core-shell (c-s), or only core (c) or shell (s). In the right column, this is further separated in the regions where the absorption takes place as indicated by the text in the legend. The coupling regime is identified as (a)-(b) enhanced absorption, (c)-(d) induced transparency, and (e)-(f) strong coupling. Figure from [128].
In Figure 6.2e-f we see the manifestations of the strong-coupling regime: A pronounced peak splitting in both scattering and absorption, and near-zero scattering intensity at resonance. This near-zero intensity is not achieved in absorption, however, as the internal losses in the dye coating are still significant.

From this analysis we can conclude that the strong-coupling regime is associated with a pronounced mode splitting in absorption as well as scattering. The criterion in Eq. (6.1.2) must still be obeyed, but in borderline cases where \( E_{\text{Rabi}} \approx \Gamma_{\text{avg}} \), the additional observation of a splitting in absorption can be used to verify the coupling regime.

### 6.2.1 MoS\(_2\) coupled to gold percolation films

When gold is deposited on a substrate, it does not cover the substrate as a fully-formed film before a certain thickness. This arises from the specific growth known as the Volmer-Weber process \([129]\). During deposition the gold atoms have stronger interaction with each other than with the substrate. Due to the high temperature, the atoms are mobile and will therefore cluster together in various nanostructures in the substrate plane. This happens until a certain thickness is reached, the percolation threshold, where they merge to form a semi-continuous thin film. For metal films, the percolation threshold is usually defined as the point where the film becomes conductive on the macroscopic scale, i.e. where it is possible to drive a current from one edge of the sample to the other. For gold on a glass substrate, this percolation threshold has been found to be between a nominal thickness of 4 and 5 nm \([130]\).

The term nominal should here be understood as the value given by the equipment from the deposition, as we can expect the nanostructures to be thicker than this due to the clustering effect. The natural nanostructures formed by these thin films and the associated plasmonic field enhancement have found applications in surface enhanced Raman scattering \([131]\), and it has been shown both in Paper A and by others that it is possible to inscribe these percolated structures with a polarization- and energy-dependent response using laser writing \([129, 130, 132]\).

Since the growth process is inherently random, a host of different plasmonic resonances can be expected from a thin film near the percolation threshold, including localised surface plasmon resonances (LSPRs), gap plasmons, and delocalised plasmonic modes as revealed by electron energy loss spectroscopy (EELS) in the case of gold on glass in Paper A. However, regular optical microscopy in the form of transmission spectra show that the overall response is represented by a broad resonance with a dip around 1.7 eV. This broadening should then be understood as a superposition of the different modes hosted by the percolation film, as previous results show good agreement between EELS and optical spectra \([133]\). The \(A\)-exciton of the TMDC MoS\(_2\) has an energy around 1.8 eV \([86]\), and it has previously been shown that it is possible to selectively enhance the photoluminescence (PL) of the different exciton species using resonance-matched metallic cavities \([134]\). As such we wished to investigate if it was possible in a similar manner to utilise the Purcell effect in these percolated gold films. Achieving this is desirable from the point of view of applications, as the percolation films are easily scalable due to their simple fabrication, and we additionally have the possibility of locally modifying the optical response as mentioned above.
6.2. Weak coupling

Figure 6.3: Average reflection (top) and photoluminescence (bottom) spectra of several MoS$_2$ flakes before (blue) and after (red) deposition of APTMS. The spectra have been normalised and shifted for clarity.

Sample fabrication

Chemical vapour deposition (CVD)-grown, monolayer MoS$_2$ flakes on c-cut sapphire from 2D Semiconductors was used as the substrate. This sample was then coated with a self-assembled monolayer in the form of 3-aminopropyl trimethoxysilane (APTMS). Using wet deposition with a solution consisting of 2.5% water, 2.5% APTMS, and 95% isopropyl alcohol results in a layer with a typical thickness of 1 nm [135, 136]. The APTMS was added as a buffer layer, as it has been shown that deposition of gold directly on MoS$_2$ results in significant quenching of the PL signal [137].

In order to ensure the optical quality of the MoS$_2$, both PL and reflection measurements were performed before and after the deposition of the APTMS layer as shown in Figure 6.3. We observe a blueshift of both the resonances of the $A$- and $B$-exciton, as well as a shift in the PL emission peak and a decrease in the intensity, but overall the quality of the flakes is preserved. This blueshift could be induced by the screening from the APTMS as discussed in the previous chapter [17], but it could also be a result of doping from the fabrication process.

The gold deposition was performed using electron beam assisted (e-beam) deposition with a rate of 0.1 nm/s. In short, e-beam deposition consists in bombarding a material target with high-energy electrons, thus transforming atoms from the target into the gaseous phase, which can subsequently be used for film deposition. The sample was divided into four regions with nominal gold thicknesses of 0, 2, 3, and 4 nm. These values below the gold percolation threshold were chosen to ensure percolated films, since APTMS has been shown to allow for smooth, fully-formed gold films with good adhesion even close to the percolation threshold [135]. Both the APTMS coating and the subsequent metal deposition were done by Johneph Sukham$^1$.

The resulting percolation films can be seen in the scanning electron microscope (SEM) images in Figure 6.4 on both the substrate (top row) and the MoS$_2$ flakes (bottom row). Curiously, the structures formed on the flakes reveal a significantly different morphology than the ones on the sapphire. On the sapphire there is a clear preference to form smaller structures, with the interconnections being formed.

$^1$PhD in the Metamaterials group headed by Assoc. Prof. Andrei V. Lavrinenko, DTU Fotonik.
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Figure 6.4: Scanning electron microscope images of percolated gold films on the sapphire substrate (top row) and the MoS$_2$ flakes (bottom row). Nominal thicknesses used in the deposition are (a)-(b) 2 nm, (c)-(d) 3 nm, (e)-(f) 4 nm. Scale bars are 100 nm.

at larger thicknesses. On the flakes we see more connected structures surrounded by smaller islands even at 2 nm. This metal clustering has been observed for silver up to a thickness of 15 nm on MoS$_2$ [138], and both these observations can be caused by the low energy barrier for gold and silver atoms to move around on the TMDC surface [139]. Surprisingly, this change in atom mobility persists even through the 1 nm APTMS layer. In any case, we still see a percolated gold film for the lowest gold thicknesses also on the MoS$_2$, which should support the previously observed broad range of plasmon modes [129].

Emission intensity dependence on gold thickness

To investigate the effect of the different percolation films on the PL emission intensity, PL and reflection spectra from five different flakes in each of the four regions were obtained. Sufficient spatial averaging of the percolation structures was ensured by using a slit width of 250 μm. For the PL spectra, the 407 nm laser with an incident power of ~5 μW was used, and both the PL and reflection measurements were obtained with a CFI TU Plan Fluor EPI 100x (0.9 NA) objective and an exposure time of 5 × 1 s each.

The resulting PL spectra can be seen in Figure 6.6a, where the spectra from the five flakes have been averaged and normalised to the intensity of the MoS$_2$ without deposited gold. Immediately obvious from the spectra is the significant decrease in emitted light as the gold thickness increases. Also seen is a broader shoulder peaked at around 1.95 eV, which comes from the gold; this is confirmed by measurements on the percolation film on the substrate alone (not shown) and the literature [137].
The quenching of the PL could be from additional nonradiative pathways introduced by the presence of the gold, as it is well-known that an emitter close to a metal surface experiences a significant decrease in the emission efficiency [140, p. 321-23]. However, if the LDOS in the plasmonic cavities was sufficiently high, the Purcell effect would reduce the lifetime of the radiative states below that of the nonradiative ones resulting in the characteristic increase in emitted light, which is clearly not the case here.

As we know from Section 3.1.2, the energy of the excitation laser is higher than the absorption edge in gold, and as such we would expect the response to be influenced by the interband transitions. Although the thickness of the gold is below the skin depth, a significant portion of the light could still be absorbed without interacting with the MoS$_2$. Since the sample was transparent, it was possible to investigate this by exciting the sample from the backside, as indicated in Figure 6.5 (but still in a reflection geometry). The result is shown in Figure 6.6b, where we see a smaller relative decrease for increasing gold thickness accompanied by a shift in the emission energy. Furthermore, we can now also see small amounts of emitted light even for the 4 nm gold, while the shoulder peak from the gold is suppressed, possibly from absorption in the MoS$_2$.

If the exciton experiences additional damping from nonradiative pathways, this will also be represented in the reflection spectra, as the exciton absorption line will broaden correspondingly. The reflection spectra are shown in Figure 6.6c-d for measurements from the front and back, respectively. Using frontside illumination, only the bare MoS$_2$ shows clear features from the A- and B-excitons. From the flakes with deposited gold we observe no significant response, not even the 2 nm region where a PL signal could otherwise be observed. Furthermore, we see an increase in the reflected signal from the 2 and 4 nm regions, but curiously the 3 nm exhibits a lower signal strength than the other regions, which could be indicative of a stronger absorption in the sample. However, we see no clear response from either the percolation film or the MoS$_2$ in any of the cases.

Looking instead at the spectra using the backside illumination, the response changes significantly from the frontside case. As before, we only observe clear features from the excitons for the bare MoS$_2$, but we now also see a broad feature with a minimum around 1.77 eV in the 2 nm region. This is shifted from the position of the bare A-exciton by $\sim$50 meV in reasonable agreement with the observed shift in the PL emission. The major increase in the feature linewidth along with the reduced emission
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Figure 6.6: Average (a)-(b) photoluminescence and (c)-(d) reflection from the (a)-(c) front and (b)-(d) back of the MoS$_2$/gold percolation film-system. All spectra have been normalised to the bare MoS$_2$ (0 nm). The legend states the nominal thickness of the deposited gold.
6.2. Weak coupling

![Figure 6.7](image)

**Figure 6.7**: Reflection spectra of the percolation film without MoS$_2$. The gold thickness is reported in the legend, and all spectra have been normalised to the bare substrate response (0 nm).

would correspond very well with the introduction of nonradiative pathways. Additionally, the intensity of the reflected light is reduced by about 50% compared to the bare case. Intuitively, the presence of the gold layer on top should increase the reflected signal through additional backscattering as was also observed in Figure 6.6c. Instead, we see a significant signal reduction for all gold thicknesses, and unless we have created a broadband region of induced transparency, this could be ascribed to increased absorption in the coupled MoS$_2$/percolation film system.

In order to further understand these phenomena, we now turn our attention to the reflection response of the percolation film directly on the sapphire substrate shown in Figure 6.7. The spectra in the case of 0, 3, and 4 nm are very similar apart from the increased signal intensity, although we see a slight dip around 1.75 eV in the 2 nm case. The strongest response by far, however, comes from the 3 nm thickness, where we observe a strong modulation of the signal compared to the bare case. Here, we see the expected broad resonance associated with the percolation film [129]. This indicates that the growth process and resulting optical response of the metal are different on APTMS than those on glass alone.

Comparing the morphology of the structures in Figure 6.4, we see a reasonable similarity between the 3 nm film on the sapphire in (c) and the 2 nm film on the MoS$_2$ in (b). The coupling of this broad feature in the percolation film with excitons in the MoS$_2$ could be responsible for the strong decrease in reflected signal observed in the backside illumination. The large discrepancy arising from the different illumination configurations would require further investigation to explain fully. However, we can still conclude that the influence of the MoS$_2$ appears to be stronger when it is at the front in the optical pathway, which can help in the design of new samples.

**Outlook**

To test if the proximity of the excitons to the metal was responsible for the decreased PL intensity, a new set of samples were made. Instead of using APTMS, a 10 nm layer of SiO$_2$ was deposited using radio-frequency sputtering at 4 mTorr of argon pressure with a power of 120 W for 2700 s, again done by Johneph Sukham. However, the oxygen plasma created by this deposition method lead to total optical degradation of the MoS$_2$. As such this method was discarded, because there is no way to perform room-temperature SiO$_2$ deposition in the cleanroom at DTU Danchip.
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To continue the investigation of coupling TMDCs and percolation films, a different sample design will be needed. Since the above results show the strongest response of the TMDC when this is positioned on top of the metal film, an inverted structure to the one depicted in Figure 6.5 could be imagined. By first depositing the metal on a substrate and subsequently covering it with a dielectric film, this system could be thoroughly characterised on its own. The optical response of the percolation film could then be optimised to allow for the best overlap with the excitons in the most suitable TMDC. Furthermore, preparing the substrate in advance would also allow for the energy- and polarisation-dependent modification using laser writing without risk of damaging the TMDC [129, 130, 132]. The monolayer TMDC flakes could then, as a first experiment, be deterministically transferred to the desired regions. Fabrication techniques have advanced to the point where the deposited dielectric thickness can be controlled on the sub-nanometer scale, which would allow for an investigation into the dependence of the MoS$_2$/percolation film distance. In addition, TMDCs can be grown directly on dielectrics [141], and it could therefore potentially be possible to fabricate these structures on a large scale in a very fast and cost-effective manner, which is an important hurdle to overcome in applications. If the decrease in reflected signal could be verified to be caused by absorption in the MoS$_2$, by e.g. measuring the photoinduced current in a gated device, this could be interesting for light harvesting, where these randomly formed metal structures have shown the possibility to enhance the absorption in a wide range of energies by a factor of 3.9 using silver and MoS$_2$ [6].
6.3 Strong coupling

Strong coupling between light and matter lies at the heart of cavity quantum electrodynamics (CQED) and has been studied for decades due to the exotic properties of these mixed light and matter states. A theoretical description of the emission of an atom in a loss-less cavity came in the early 1980s [142], and predictions of systems where this splitting could be observed experimentally soon followed [143, 144]. The observation of coherent energy exchange between the mixed states, i.e. the Rabi oscillations, was observed shortly thereafter [145]. The mode splitting in various microwave cavities was experimentally verified in the following years [146, 147], culminating with the observation of mode splitting between, on average, a single caesium atom in an optical cavity [148]. These advances opened a new regime in CQED, where the spatial trajectory of single atoms was mapped in real-time via the strong nonlinear response of the atom-cavity coupled system to external fields [149].

Further advances in the field of QED allowed for trapping atoms in cavities, where the strong nonlinearity of the system was employed to demonstrate a single-atom laser [150]. Furthermore, with the advances in fabrication techniques came the possibility to make high quality factor (Q-factor) dielectric cavities. During the growth of these structures it was possible to incorporate single quantum dots inside, which was realised in the form of micropillars [25], photonic crystal cavities [26], and microdisks [151]. These solid-state systems had small Rabi splittings on the order of $\sim 200 \, \mu\text{eV}$, but the strong-coupling regime was achieved nonetheless due to the narrow linewidths of the system constituents.

In that perspective history is repeating itself after the successful isolation of few- to monolayer 2D materials. The strength of the excitonic response in these new material platforms has allowed for the observation of the strong-coupling regime in dielectric cavities [19, 20]. However, there is a crucial difference between the results obtained previously and now, namely that the excitons in 2D materials are stable at ambient conditions. Trapped atoms and quantum dots all require cryogenic or even liquid helium temperatures to stabilise the modes and reduce the dephasing from the environment. On the other hand, they do have in common that the attained coupling strength is inhibited by the cavity mode volume, since the coupling strength depends on the mode volume as $g \propto V^{-1/2}$, as we know from Eq. (6.1.1). For dielectric cavities, the mode volume is diffraction limited to $V \sim (\lambda/n)^3$, where $\lambda$ is the cavity resonance wavelength, and $n$ is the refractive index.

For this reason, plasmonic resonances have become of great interest to use as the cavity modes. As we saw in Chapter 3, plasmons have the ability to confine the electromagnetic field on a deep sub-wavelength scale beyond the diffraction limit, and the associated field enhancement further strengthens the coupling. In addition, the plasmonic resonance energy is controllable through the morphology and material of the cavity [152], allowing it to be resonance matched to a variety of emitters. These qualities have previously allowed for the observation of the strong-coupling regime in systems with plasmons coupled to organic and inorganic compounds [27, 28, 153–157]. Although the damping of the plasmon mode is significantly larger than for e.g. a micropillar (typically on the order of 150 meV), the field confinement and enhancement remedies this by enabling Rabi splittings in the 100s of meV.

Combining the attractive features of plasmonic cavities with those of the TMDCs has gained increased attention in recent years [119, 158]. The coupling to the excitons has been realised in various geometries, such as plasmonic cavities [101, 104, 126],
plasmonic lattices [159, 160], and single nanoparticles [10, 109, 161]. Due to their stability, it has even been possible to experimentally realise coupling between the trions in WS\(_2\) and single nanoparticles, although at liquid helium temperatures [162]. The chirality of the TMDCs discussed in Section 4.1.1 can furthermore be used to couple to chiral plasmonic modes with high selectivity [98].

In the early experiments, the obtained Rabi splittings were in the MHz regime giving rise to oscillations on a timescale of 100s of nanoseconds and as such were easily measurable. However, a Rabi splitting of 100 meV produces drastically faster oscillations on the order of 10s of femtoseconds [153], which complicates the detection of the coherent energy exchange. Resolving these ultra-fast processes have been accomplished using pump-probe spectroscopy [153]. This provides us with a deeper understanding of the system dynamics, which is an important step towards applications of the strongly coupled systems.

After this introduction to the fascinating field of strong coupling, we will now take a closer look at more specific theoretical models that will enable us to calculate the response of a coupled system. Since a major part of the work in this PhD has been focused on coupling excitons in TMDCs with plasmons in various metallic structures, in the following we will use the subscript "pl" for the LSPR constituting the plasmonic cavity, and "ex" for the exciton representing the two-level emitter.

6.3.1 The coupled-oscillator model

Equations of motion

In order to fit individual experimental spectra, an expression for the scattering spectrum of the coupled system is needed. In the following we will use the phenomenological coupled-oscillator model (COM) to obtain this expression, which has previously been used to successfully describe the coupling of quantum dots with metallic nanoparticles [163]. Before beginning, we note that this model is not intended to accurately represent the underlying physics but merely to describe the observed behaviour, although it can be shown to be equivalent to a quantum-mechanical resonator coupled to a two-level system, as long as the two-level system is only weakly excited [163].

We describe both the exciton transition and LSPR as a damped harmonic oscillator, where the oscillations represent the polarisation of the two constituents. They are coupled through the electric near-field with the coupling strength \( g \), which yields the two equations of motion

\[
\begin{align*}
\ddot{x}_{\text{pl}}(t) + \Gamma_{\text{pl}} \dot{x}_{\text{pl}}(t) + E_{\text{pl}}^2 x_{\text{pl}}(t) + g \dot{x}_{\text{ex}}(t) &= F_{\text{pl}}(t), \\
\ddot{x}_{\text{ex}}(t) + \Gamma_{\text{ex}} \dot{x}_{\text{ex}}(t) + E_{\text{ex}}^2 x_{\text{ex}}(t) + g \dot{x}_{\text{pl}}(t) &= F_{\text{ex}}(t),
\end{align*}
\]

(6.3.1)

(6.3.2)

where \( x_{\text{pl,ex}} \) are the coordinates of the plasmon and exciton oscillation, respectively, \( E_{\text{pl,ex}} \) and \( \Gamma_{\text{pl,ex}} \) are the plasmon (exciton) energy and linewidth, respectively, and \( F_{\text{pl,ex}} \) are the forces from the external electromagnetic field driving the oscillations. To obtain an analytical solution, we assume the extinction of the plasmonic mode is much larger than that of the exciton, since LSPRs are associated with a strong optical response compared to excitons [164]. From this we have \( F_{\text{pl}} \gg F_{\text{ex}} \), and we therefore set \( F_{\text{ex}} \approx 0 \). Assuming harmonic time-dependence of the external field, it can be
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Shown that the scattering cross section of the coupled system is given by [163]

$$\sigma_{\text{scat}}(E) \propto E^4 \left| \frac{(E_{\text{ex}}^2 - E^2 - i\Gamma_{\text{ex}}E)}{(E^2 - E_{\text{pl}}^2 + i\Gamma_{\text{pl}}E)(E^2 - E_{\text{ex}}^2 + i\Gamma_{\text{ex}}E) - E^2 G^2} \right|^2. \tag{6.3.3}$$

This explicit form of the scattering cross section allows us to investigate the influence of varying the different parameters individually. Choosing a set of representative values results in the spectra shown in Figure 6.8, where all parameters are varied in turn apart from the exciton energy, which was kept constant at $E_{\text{ex}} = 1.98 \text{ eV}$. With the parameters used, we calculate a Rabi splitting of $E_{\text{Rabi}} = 120 \text{ meV}$ (cf. Eq. (6.3.9)) indicative of the strong-coupling regime since $E_{\text{Rabi}} > \Gamma_{\text{avg}} = 100 \text{ meV}$ from Eq. (6.1.2). As such, we refine the hallmark of a strongly coupled system in the form of a distinct mode splitting.

Starting with the plasmon energy $E_{\text{pl}}$ in Figure 6.8a, we see a clear shift in the spectral weights as $E_{\text{pl}}$ is tuned across $E_{\text{ex}}$. Exactly on resonance, where $E_{\text{pl}} = E_{\text{ex}}$, there is an almost equal weight in the two peaks with a slight shift towards the high-energy peak. This way of varying the energy of one of the coupled-system constituents allows for the extraction of the upper and lower polariton branch (UPB and LPB) as a function of the energy detuning, which in turn can be used to map out the dispersion and thus determine the Rabi splitting of the system.

Varying instead the coupling strength $g$ in Figure 6.8b, we see the direct impact in a larger peak separation as well as more pronounced dip in the spectra reaching near-zero intensities at the position of the exciton energy. A similar trend is observed for the exciton linewidth in Figure 6.8c: As $\Gamma_{\text{ex}}$ is increased the dip becomes much less pronounced, although this time the peak separation increases as the dip diminishes.

Finally, as the plasmon linewidth $\Gamma_{\text{pl}}$ is increased, we see an increase in the overall width of the spectrum as well as the peak separation, but with little influence on the magnitude of the dip.
For the three latter cases, the ratio of the spectral weights between the two peaks is preserved with the slightly larger weight in the high-energy peak. Additionally, we see that the position of the dip corresponds to the exciton energy in all cases, with a slight change in the very detuned spectra in Figure 6.8a.

Fitting Eq. (6.3.3) to experimental data yields the result shown in Figure 6.9. Here, the plasmonic cavity is comprised of a thin gold nanodisk, the same as was used in Paper B, while the two-level emitter takes the form of excitons in monolayer WS\textsubscript{2}. Despite the phenomenological origin of the COM, we see excellent agreement between the experiment and the theory, which in principle allows for the extraction of the relevant parameters. However, since we are working in a five-dimensional parameter space, where each individual parameter influences multiple aspects of the spectrum, unique and simultaneous determination of them all from a single spectrum is subject to significant uncertainty. Furthermore, the exact value of each parameter is expected to vary for different cavities (i.e., nanoparticles) due to the specific morphology and surroundings of the individual systems.

In most cases we are interested in the average system response under similar conditions, i.e., similar particles, exciton response, etc., that can not be expected to be identical due to the microscopic variations. In the following, we will therefore see how this average response can be determined by using a Hamiltonian description of the COM. This enables incorporation of the statistical variations from individual spectra in order to determine a system average of the interesting parameter, namely the coupling strength.

**Hamiltonian form**

Instead of calculating the individual spectra, the COM can also be represented in a matrix formulation, where two states of different energies and linewidths are coupled through an off-diagonal element representing the coupling strength. In its non-Hermitian form, the matrix representation of the COM is given by the eigenvalue problem \[165\]

\[
\begin{pmatrix}
E_{\text{pl}} - i\frac{\Gamma_{\text{pl}}}{2} & g \\
g & E_{\text{ex}} - i\frac{\Gamma_{\text{ex}}}{2}
\end{pmatrix}
\begin{pmatrix}
\alpha \\
\beta
\end{pmatrix}
= E_{\pm}
\begin{pmatrix}
\alpha \\
\beta
\end{pmatrix}
,\tag{6.3.4}
\]

\[68\]
where $E_{pl}$ and $\Gamma_{pl}$ are the plasmon energy and linewidth, $E_{ex}$ and $\Gamma_{ex}$ are the exciton energy and linewidth, $g$ is the coupling strength, and $\alpha$ and $\beta$ are the Hopfield coefficients which describe the relative contribution of the plasmon ($\alpha$) and exciton ($\beta$) in the polariton [166]. To obtain the energy eigenvalues $E_{\pm}$ we need the real part of $E_{\pm}$.

In order to plot the eigenvalue spectrum in Eq. (6.3.7), and fit it to experimental data, we need the real part of $E_{\pm}$. To find this we use the following identity for the square root of a complex number

$$\sqrt{a + ib} = \frac{1}{\sqrt{2}} \left( \sqrt{a^2 + b^2} + a + i \text{sgn}(b) \sqrt{a^2 + b^2 - a} \right)$$

From the eigenvalue spectrum in Eq. (6.3.8) we see the existence of two solutions: The UPB ($E_+$) and the LPB ($E_-$), which are plotted in Figure 6.10a-b for varying $g$ and $\Gamma_{pl}$, respectively.

From the eigenvalue spectrum in Eq. (6.3.8) we see the existence of two solutions: The UPB ($E_+$) and the LPB ($E_-$), which are plotted in Figure 6.10a-b for varying $g$ and $\Gamma_{pl}$, respectively. As can be seen, increasing the coupling strength and decreasing the plasmon damping increases the distance between the two branches, but the effects are somewhat interchangeable between different parameters as we also saw in Figure 6.8. Exactly at zero detuning we find an explicit expression for the Rabi splitting, defined as the energy difference between the UPB and LPB:

$$E_{Rabi} = (E_+ - E_-)_{\delta=0} = \sqrt{4g^2 - \frac{\left(\Gamma_{pl} - \Gamma_{ex}\right)^2}{4}},$$  

(6.3.9)
which is the typical figure of merit (FOM) for these electromagnetically coupled systems. Looking at Eq. (6.3.9), we see that by matching the plasmon and exciton linewidths while maximizing $g$ leads to the highest attainable Rabi splitting. As described earlier in Eq. (6.1.2), however, the criterion for entering the strong-coupling regime is 
$$E_{\text{Rabi}} > \Gamma_{\text{avg}} = (\Gamma_{\text{pl}} + \Gamma_{\text{ex}})/2,$$
which means that the Rabi splitting alone does not adequately describe the system. To better reflect the properties of the system and allow for comparison between different realisations of the strong-coupling regime, another FOM could be the quantity
$$\text{FOM} = E_{\text{Rabi}} / \Gamma_{\text{avg}},$$
(6.3.10)
since this parameter in addition to the Rabi splitting also takes the system damping into account. A contour plot of Eq. (6.3.10) is depicted in Figure 6.11a for $g = 60 \text{ meV}$; the dashed line indicates FOM = 1 separating the two coupling regimes.

From the figure it is immediately obvious that the largest FOM is attained by simultaneously minimizing both of the linewidths, with no preference on either of the two. Another commonly used measure for the performance in the CQED community is the cooperativity given by $C = 4g^2 / \Gamma_{\text{ex}} \Gamma_{\text{pl}}$ [167–169]. However, as this value is not typically reported in the works employing TMDCs, we will use the one defined in Eq. (6.3.10) for comparison with these, and reserve the cooperativity for perspective purposes.

Fitting Eq. (6.3.8) to experimental data allows for simultaneous determination of the energies, linewidths and the coupling constant. However, as mentioned in the discussion of Eq. (6.3.3), fitting five parameters to a set of data always begets a certain uncertainty, especially with an expression as involved as Eq. (6.3.8) and the ambiguity in the parameter interconnection as shown in Figure 6.8. Fortunately the only truly unknown in practice is the coupling strength $g$. The exciton energy and linewidth are (ideally) constants which can be obtained from absorption measurements of a bare 2D flake, i.e. without any particles as we did in Section 4.3.3, although we note that the local exciton energy is subject to variations induced by the fabrication process required to couple the TMDC with the plasmonic cavity, as discussed in Paper B. Still, the bare exciton energy is typically taken as representative, and with this the plasmon energy can be deduced from energy conservation via the relationship
$$E_{\text{pl}} + E_{\text{ex}} = E_+ + E_-,$$
(6.3.11)
where $E_+$ and $E_-$ can be obtained from the experimental spectra as the peak positions. The plasmon linewidth is typically determined from measurements of similar particles on a substrate without the presence of the 2D material. This does lead to another degree of uncertainty as the spectrum of a plasmonic particle is highly dependent on the specific geometry especially around regions with the highest field enhancement (e.g. the tips of triangle), and the altered dielectric environment of the 2D material will also change the plasmonic resonance. Unique identification of the individual plasmon dampings would be preferred, although it is in practice difficult to accomplish.

With the eigenvalues and the procedure for obtaining the coupling strength determined, we can now examine the Hopfield coefficients to gain further insight into the
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Figure 6.10: Plot of the eigenenergies from the coupled-oscillator model. Parameter values used are $E_{\text{ex}} = 1.98 \, \text{eV}$, $\Gamma_{\text{ex}} = 50 \, \text{meV}$, (a) $\Gamma_{\text{pl}} = 150 \, \text{meV}$, and (b) $g = 100 \, \text{meV}$.

The physical nature of the polaritonic states. Using the top equation from the Hamiltonian in Eq. (6.3.4) yields

$$
\beta_{\pm} = \frac{1}{g} \left( E_{\pm} - E_{\text{pl}} + \frac{i}{2} \Gamma_{\text{pl}} \right) \alpha_{\pm}
= \frac{1}{g} \left( -\frac{1}{2} \delta + \frac{i}{4} \left( \Gamma_{\text{pl}} - \Gamma_{\text{ex}} \right) \pm \sqrt{g^2 + \frac{1}{4} \left[ \delta - \frac{i}{2} \left( \Gamma_{\text{pl}} - \Gamma_{\text{ex}} \right) \right]^2} \right) \alpha_{\pm}
= k_{\pm} \alpha_{\pm} .
$$

From Eq. (6.3.12), and by demanding that the Hopfield coefficients satisfy the relation $|\alpha_{\pm}|^2 + |\beta_{\pm}|^2 = 1$, we can obtain explicit expressions for the two:

$$
|\alpha_{\pm}|^2 = \frac{1}{1 + |k_{\pm}|^2} , \quad (6.3.13)a
$$
$$
|\beta_{\pm}|^2 = \frac{1}{1 + |k_{\pm}|^{-2}} . \quad (6.3.13)b
$$

Plotting Eq. (6.3.13)a-b in Figure 6.11b reveals that the polaritonic state in the upper (lower) branch is predominantly exciton-like (plasmon-like) for large negative detunings. As the energy of the plasmon approaches that of the exciton, the two branches approach each other and the states mix increasingly achieving a 50/50 composition exactly at $\delta = 0 \, \text{meV}$. Following this they veer off again, and the upper (lower) branch becomes predominantly plasmon-like (exciton-like). This evolution can also be inferred from the two branches of the dispersion in Figure 6.10, where the UPB and LPB are closer in energy to that of the bare exciton and plasmon at negative detunings, respectively. As $\delta$ tends to zero, the UPB and LPB reach an equidistance from the bare energies, after which separate again and asymptotically approach the bare exciton (for the LPB) and plasmon (for the UPB) energy.

With this analysis complete we can now identify a part of the attractiveness of these strongly coupled systems both for science and applications. In the strong-coupling regime, energy in the coupled system cycles back and forth between the two states faster than any damping processes, which means the energy is stored in the system.
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Figure 6.11: (a) Contour plot of the figure of merit $E_{\text{Rabi}}/\Gamma_{\text{avg}}$, where $\Gamma_{\text{avg}} = (\Gamma_{\text{pl}} + \Gamma_{\text{ex}})/2$, showing the two coupling regimes for $g = 60 \text{ meV}$. The lower left area represents strong coupling as per the criterion $E_{\text{Rabi}}/\Gamma_{\text{avg}} > 1$, while the upper right indicates weak coupling. The dashed line shows the border value 1. (b) Evolution of the Hopfield coefficients with the detuning. Top: $\alpha_{\pm}$ (plasmon component), bottom: $\beta_{\pm}$ (exciton component).

Figure 6.12: Sketch of the coupled plasmon/exciton system. The TMDC flake hosting the exciton is exfoliated on an SiO$_2$/Si substrate, and the metallic nanodisk with the localised surface plasmon resonance is deposited on the flake.

for a number of cycles before being reemitted or lost to nonradiative pathways. Furthermore, as the detuning tends to 0 meV the states become a coherent 50/50 mix of light and matter as shown by the Hopfield coefficients. Since matter is inherently easier to manipulate than light, this allows for the possibility to manipulate the light by influencing the matter before the light is reemitted. Besides the advantages of being able to address the strong-coupling regime at ambient conditions using TMDCs and the plethora of interesting, basic physics associated with it, coherent manipulation of light has a multitude of applications e.g. for low-threshold lasers, chemical reaction promotion, and quantum information processing down to the single qubit limit [170].

With the underlying, albeit basic, theory in place, we can now turn our attention towards the experimental realisation of the coupled plasmonic cavity/exciton system.

6.3.2 Experimental realisation of coupled plasmon/exciton systems

As described in the introduction, strong coupling has been realised in many different systems. In the following we will focus on the coupling between an open plasmonic cavity in the form of a gold nanodisk, and excitons in the TMDCs WSe$_2$ and WS$_2$. 
6.3. Strong coupling

Before looking at the experimental results for the individual systems, we will cover some common features between the two.

The TMDC flakes were exfoliated by Lene Gammelgaard and Bjarke Jessen on a silicon substrate with a thermally grown oxide layer. The multiple internal reflections in the oxide layer enhance the contrast significantly [105], and this allows for automated detection of different layers using quantitative optical mapping [171]. Exfoliated flakes were chosen over CVD-grown as these are of the highest optical quality and thus should enable stronger coupling to the nanodisks.

The gold nanodisks were synthesised by Ximin Cui. Briefly, the synthesis uses a seed-mediated method which produces single-crystalline nanoplatelets (triangles) [152]. Subsequent oxidation primarily etches under-coordinated atoms at the corners, resulting in gold nanodisks of the same thickness as the platelets. By careful control of the process parameters, it is possible to fabricate nanodisks with a desired size and thus LSPR energy. Furthermore, the chemical synthesis naturally caps the surface of the nanodisks with a thin layer (around 1 nm) of cetyltrimethylammonium bromide (CTAB), which hinders direct contact between the metallic particle and the TMDC and thus limits quenching.

The nanodisk solution was prepared for deposition by centrifugation to remove organic residues in the liquid (see Appendix B for details). The prepared solution was then dropcasted on the sample, left for an amount of time typically around 60 s, and then removed by blowing with N₂. As we saw previously, we need to be able to tune the energy of one constituent, exciton or plasmon, relative to the other in order to map out the dispersion of the coupled system. Fortunately, the synthesis process does not produce only particles of a given size, but rather a distribution centred around a controllable mean. This size distribution allows for such a tuning, as the natural variation exactly produces particles with different LSPR energies. As the dropcast method is inherently random, the sample preparation will thus facilitate measuring the full dispersion if a sufficient amount of coupled nanodisks can be sampled.

6.3.3 First results with gold nanodisks on WSe₂

When this project started, no experience on these coupled systems was present in the group, and the work on exfoliating TMDCs had just been started by our collaborators. At this early stage, WSe₂ proved simpler to exfoliate into large flakes, which is necessary to increase the likelihood of successful particle deposition. We furthermore had the opportunity to initiate a collaboration with Prof. Jianfang Wang and his PhD student Ximin Cui regarding the gold nanoparticles, as they were visiting DTU at the time. For their visit, they had brought synthesised particles in the form of single-crystalline gold nanodisks. Choosing to work with what was at hand, the first system realised was therefore these nanodisks coupled to a WSe₂ monolayer as shown in Figure 6.13.

Darkfield measurements were performed on all the particles using a CFI TU Plan Fluor EPI 100x (0.9 NA) objective and an exposure time of 10 × 1 s. An example spectrum can be seen in Figure 6.14a, where the observation of a dip in the scattering spectrum was a huge encouragement from this first experiment. Fitting the COM
allowed for the extraction of the relevant parameters, although as described earlier with significant uncertainties. This resulted in an exciton energy and linewidth of $E_{\text{ex}} \sim 1.64 \text{ eV}$ and $\Gamma_{\text{ex}} \sim 25 \text{ meV}$, respectively, and an average linewidth of the nanodisks of $\Gamma_{\text{pl}} \sim 300 \text{ meV}$. Subsequent analysis of the data resulted in the dispersion shown in Figure 6.14b, from which we can infer a splitting of $E_{\text{Rabi}} \sim 95 \text{ meV}$. As the average linewidth of the coupled system is $\Gamma_{\text{avg}} \sim 163 \text{ meV}$, we clearly see the system is in the weak-coupling regime, which is also evident from the magnitude of the dip in the scattering spectrum. Using the terminology from earlier [128], the coupled system is most likely in the regime of enhanced absorption, where the increased electric field from the plasmonic resonance promotes energy dissipation in the WSe$_2$.

Furthermore, from the dispersion we can conclude that the distribution of particles used was not sufficiently resonance matched to the $A$-exciton in WSe$_2$. All the measurements included in the dispersion are detuned to higher energies, and indeed, a comparison between Figure 6.13 and 6.14b reveals that only 40% of the particles showed any signs of coupling because of this energy mismatch.

Finally, the shape of the gold nanoparticles from this synthesis was by inspection in SEM images found to have shapes ranging from platelets over truncated triangles
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and hexagons to disks. The mode distribution of a platelet and a disk is very different, and as such it is difficult to draw any certain conclusions about the performance of the system, since the term "system" here is ill-defined.

6.3.4 Ultra-thin, single-crystalline gold nanodisks on WS$_2$

Based on the initial results above, it was clear that optimisation of the coupled system was needed in order to reach the strong-coupling regime. In the following, we will give a brief overview of the thoughts behind the choices leading to the results in Paper B, as well as a summary of the main results.

Starting with the 2D material, we made the choice to change to WS$_2$, as the larger transition dipole moment and the higher energy of the $A$-exciton would both serve to increase the coupling strength as seen in Eq. (6.1.1) [119, 128].

Concerning the open plasmonic cavity, it was obvious that a better spectral overlap between the plasmon and exciton resonance as well as a reduction in the LSPR linewidth was necessary. To incorporate both of these considerations, we changed the particles to a thinner version of the previously used single-crystalline gold nanodisks, where a new batch of particle solutions over a broad range of mean LSPR energies were made.

To enable better spectral overlap between the LSPR and exciton energies, trial depositions were done on an SiO$_2$/Si substrate similar to the one used for exfoliation. As we know from Section 3.2.2, the LSPR resonance is sensitive to the dielectric constant of the surrounding medium, and since the nanodisks were supplied in solution, the effect of the change of surroundings had to be gauged. Taking this into account led to the use of nanodisks with a radius on the order of $R = 30$ nm, where the aforementioned size variation would allow us to determine the dispersion relation of the coupled system.

The decreased thickness to $8.8 \pm 0.2$ nm as measured without the CTAB molecule facilitated a reduction of the average LSPR linewidth of the used particles to 170 meV, which gives a $Q$-factor of the plasmonic cavity of 11.5. This represents a significant improvement from previously, where $Q \sim 5.5$, and it is close to a theoretical prediction of the maximum $Q$-factor of 13.5 for a plasmonic particle of arbitrary shape in the quasi-static limit [172], thus showing reduced damping from surface scattering and defects. Furthermore, the small thickness of the particles and the strong in-plane dipole moment of the LSPR should enable good overlap with the dipole moment of the 2D exciton in WS$_2$ [126, 152].

All darkfield and brightfield measurements presented in the following was obtained using a CFI TU Plan Fluor EPI 100x (0.9 NA) objective and an exposure time of $3 \times 5$ s and $5 \times 0.1$ s for the dark- and brightfield, respectively. The slit width was set to 100 µm to reduce the influence of the background signal as much as possible.

Monolayer coupling

From the considerations above, new samples were made where resonance-matched, high $Q$-factor single-crystalline gold nanodisks were deposited on monolayer WS$_2$ flakes. Darkfield scattering and brightfield reflection spectra were obtained for the particles, which were subsequently checked with SEM images to ensure the particle morphology was cylindrical; differently shaped particles and dimers were at this
stage removed from further analysis. SEM images of five selected nanodisks can be seen in Figure 6.15d.

The exciton energy and linewidth was determined from reflection measurements, where the dielectric function of the WS₂ was extracted using the transfer-matrix method as described in Section 4.3.3. From this we obtain the values $E_{\text{ex}} = 1.963 \text{eV}$ and $\Gamma_{\text{ex}} = 28 \text{meV}$, while from the measurements of the nanodisks on the bare SiO$_2$/Si substrate we have the average plasmon linewidth $\Gamma_{\text{pl}} = 170 \text{meV}$. The dispersion of the coupled system is then constructed by extracting the energy of the UPB and the LPB from each individual scattering spectrum of the nanodisk coupled to the WS₂. Using energy conservation in Eq. (6.3.11) gives us the plasmon energy, from which we can calculate the detuning $\delta = E_{\text{pl}} - E_{\text{ex}}$ and thus plot the extracted positions of the UPB and LPB as a function of the detuning.

![Figure 6.15:](image)

The result can be seen in Figure 6.15a, where we clearly see the avoided crossing characteristic for these coupled systems [25, 109]. The vertical error bars come from the uncertainty in extracting the peak positions, which was estimated to $\pm 5 \text{meV}$. The horizontal error bars represent the propagated measurement uncertainty dominated by the variation in the measured exciton energy.

As described, we have determined all parameters with other methods in the COM save the coupling strength $g$. Simultaneously fitting the real part of the energy spectrum given by the COM in Eq. (6.3.8) to the UPB and LPB yields $g = 64 \pm 3 \text{meV}$, which results in a Rabi splitting of $E_{\text{Rabi}} = 108 \pm 8 \text{meV}$. Since $\Gamma_{\text{avg}} = 99 \pm 3 \text{meV}$,
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we obtain using Eq. (6.3.10) an FOM of $E_{Rabi}/\Gamma_{\text{avg}} = 1.09 \pm 0.08$ and can therefore conclude that the coupled system is in the strong-coupling regime.

To further validate this, we turn our attention to the scattering and reflection spectra in Figure 6.15b and 6.15c. Akin to the evolution observed in the COM in Figure 6.8a, we see a shift of spectral weight in the scattering spectra from the LPB to the UPB as the detuning increases from negative to positive. As discussed earlier, however, strong coupling is associated with a splitting not only in the scattering spectrum, but also in the absorption \[128\], although measuring the absorption directly requires special techniques \[32, 33\], which we did not have access to.

In these samples, we addressed this by performing reflection measurements in addition to the scattering. As depicted in Figure 6.16, the raw reflected signal, $R_{\text{raw}}$, contains contributions from multiple sources: The direct and multiple internal reflections of the uncoupled WS$_2$, $R_{\text{WS}_2}$, as well as scattering and absorption from the coupled nanodisk/WS$_2$-system. As suggested by the finite-element method calculations\[4\] seen in Figure 6.17a, the absorption cross section of these nanodisks is more than an order of magnitude larger than the scattering cross section. From this we can infer that a part of the reflection spectrum $R_{\text{raw}}$ will be comprised of the absorption properties of the coupled system.

However, the response from the uncoupled WS$_2$ spectrum will dominate the spectrum, if this background is not carefully corrected for. The optical response of the WS$_2$ should be uniform as governed by the material properties, but as we saw already in the case of pristine, exfoliated flakes in Section 4.3.3, variations occur due to e.g. local strain and substrate doping \[116\]. Additional doping from the nanodisk solution increases this spread in material parameters further as discussed in Paper B. But because the 2D nature of the CCD allows for local extraction of the background signal as described in Section 2.3.1, we are able to obtain and subtract the correct background spectrum for each nanoparticle individually. We therefore define the reflection spectrum as

$$
\Delta R = \frac{R_{\text{WS}_2} - R_{\text{raw}}}{R_{\text{sub}}}, \quad (6.3.14)
$$

where $R_{\text{sub}}$ is the reflection of the bare SiO$_2$/Si substrate. Although the substrate response is almost non-dispersive over the energy range of interest, we use this definition to take the additional contribution into account. The reflection spectra obtained in this manner are shown in Figure 6.15c for the same five particles as in 6.15b. Here we observe a similar shift in the spectral weights between the UPB and LPB as for the scattering when $E_{\text{pl}}$ is varied across $E_{\text{ex}}$. Furthermore, we see a consistent blueshift

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\[4\]See the Methods section in Paper B for details.
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Figure 6.17: (a) Scattering (red) and absorption (blue) cross sections $\sigma$ of a nanodisk of radius $R = 23$ nm calculated using the finite-element method. The cross sections have been normalised to the geometrical area, while $\sigma_{\text{scat}}$ has been multiplied by 50 to match. The ratios between the maxima of $\sigma_{\text{abs}}$ and $\sigma_{\text{scat}}$ vary from 96 down to 21 when going from a nanodisk radius of $R = 19$ nm to $R = 29$ nm. (b)-(c) Normalised $\sigma_{\text{scat}}$ and $\sigma_{\text{abs}}$ of nanodisks with radii $R = 19$ nm, 23 nm, 25 nm, 27 nm, and 29 nm, arranged from top to bottom. The calculations were done by Nicolas Stenger.

of the reflection compared to the scattering, which we also observed in the case of absorption and scattering for spherical gold particles in Figure 3.7b. This corroborates our interpretation of the reflection spectra as containing information about the absorption properties of the coupled system. The observation of mode splitting and the spectral evolution in reflection strengthens our conclusion of the observation of the strong-coupling regime in this system.

In addition to estimating the relative magnitude of the absorption and scattering cross sections, we can use the results from the calculations to compare the numerically predicted mode splitting with that obtained experimentally. In Figure 6.17b-6.17c we see the calculated spectra for the coupled system, which agree very well with their experimental counterparts. From Figure 6.15d we see that the largest nanoparticle measured has a radius of $R \sim 35$ nm, whereas the largest in the calculation has $R = 29$ nm. However, as described in Section 3.1.1 the skin depth of gold is $\sim 25$ nm at an energy of $1.96$ eV \cite{38}. As such the electric field completely permeates the nanodisk with its thickness of only 8.8 nm, and we must expect the optical response to be critically dependent of the dielectric function used in the calculations, as we also show in the Supplementary Information of Paper B. Combining this with the challenges associated with the background removal discussed in Section 2.3.1, we can reasonably account for the discrepancies between experiment and calculations.

Performing the same analysis of extracting the peak positions of the UPB and LPB yields the black crosses indicated in Figure 6.15a, where we see an excellent agreement between the predicted Rabi splitting and the measured.

Comparing the FOM obtained here of 1.09 ($E_{\text{Rabi}} = 108$ meV) with literature values, we see similar FOMs for systems comprised of plasmonic cavities and TMDCs: Results from Wen et al. \cite{10} yields an FOM of 1.03 (106 meV), Han et al. \cite{101} reported 1.07 (145 meV), while Stührenberg et al. \cite{109} achieved 1.07 (83 meV). As such we
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Figure 6.18: Experimentally determined dispersion for the coupled nanodisk/multilayer WS\(_2\)-system. The solid lines are again fits to the coupled-oscillator model, and the solid crosses indicate the extracted peak positions from finite-element method calculations. Note the difference in the scale of the y-axis as compared to Figure 6.15a.

see that this nanodisk/WS\(_2\)-system performs slightly better in the monolayer case than similar systems, although this increase is within experimental uncertainties.

Rabi splitting increase through multilayer coupling

From the exfoliation process, not only monolayers are obtained; in fact, the monolayers are the exception rather than the norm. Since the dropcast method for depositing the nanodisks is an inherently large-scale (compared to the size of the flakes) and random process, the particles will also be deposited on the multilayers. It has been shown that by increasing the number of layers participating in the coupling, it is possible to increase the Rabi splitting of the system [109, 126, 173]. This increase is ascribed to the additional overlap of the plasmonic mode with the excitonic material, as well as increased overlap of the direction of the electric field with the dipole orientation of the exciton, since interlayer excitons can form in multilayer TMDCs giving an out-of-plane dipole moment [126].

To investigate this effect in our system, we identified a flake with a height of 4.4 nm corresponding to seven layers of WS\(_2\), where the nanodisks had also been deposited. The optical properties of the A-exciton in the multilayer flake were determined to be \( E_{\text{ex,multi}} = 1.942 \text{ eV} \) and \( \Gamma_{\text{ex,multi}} = 44 \text{ meV} \), again by using the transfer-matrix method on reflection spectra.

Following the same procedure as for the monolayer case with darkfield measurements and subsequent data analysis allows us to map the dispersion. The result is shown in Figure 6.18, where we again see good agreement with the theoretically calculated results indicated by the black crosses. We do observe a lower Rabi splitting from the calculations, however, which could be caused by the fact that we treat the WS\(_2\) as an in-plane isotropic material and therefore do not take the out-of-plane response into account. From the experimental dispersion we extract a coupling strength of \( g_{\text{multi}} = 93 \pm 4 \text{ meV} \) and a Rabi splitting of \( E_{\text{Rabi,multi}} = 175 \pm 9 \text{ meV} \). These values represent an increase relative to the monolayer values of 45 % and 62 %, respectively, while with \( \Gamma_{\text{avg,multi}} = 107 \pm 3 \text{ meV} \) the FOM increases to 1.64 ± 0.08, representing an increase of 50 %.
Comparing this FOM to literature values again, we see that Stührenberg et al. [109] reached 1.17 (\(E_{\text{Rabi}} = 101\) meV), Kleemann et al. [126] got 1.47 (140 meV), and Wang et al. [173] found 1.57 (100 meV). As we see from this and the discussion in the monolayer case, the FOM better represents the system, as the distinguishability of the UPB and LPB more adequately describes the performance. Furthermore, we can conclude that the coupling in our multilayer \(\text{WS}_2\)/nanodisk system is the strongest reported between an open plasmonic cavity and a TMDC both in terms of this FOM and the actual Rabi splitting.

**Coupling dependence on temperature**

In the previous, we used the inherent variation of the nanodisks’ size to obtain the dispersion relation. However, other methods have also been used to realise the detuning, e.g. in the case of adding additional dielectric material on a single silver nanorod to redshift the LSPR [31], by electrically gating the TMDC [10], and also by varying the temperature to shift the exciton resonance energy [10, 174, 175]. This change in the exciton energy happens because semiconductor bandgaps in general vary with the temperature according to the modified Varshni equation [176]

\[
E_g(T) = E_g(0) - S \langle \hbar \omega \rangle \left( \coth \left( \frac{\langle \hbar \omega \rangle}{2k_B T} \right) - 1 \right),
\]

(6.3.15)

where \(E_g(0)\) is the bandgap at zero temperature, \(S\) is a dimensionless constant representing the electron-phonon interaction strength, \(\langle \hbar \omega \rangle\) is the average phonon energy involved in these interactions, and \(k_B\) is the Boltzmann constant. This has previously been successfully applied to describe the redshift of PL emission energy of TMDCs for increasing temperature [177, 178], where the agreement of the observed energy shift and the Varshni equation indicates that the binding energy of the excitons vary little with temperature.

All spectra presented in the following were obtained using a CFI TU Plan BD ELWD 50x (0.6 NA) objective and an exposure time of 3 \(\times\) 0.1 s and 3 \(\times\) 5 s for the reflection and scattering measurements, respectively.

Before looking at the coupled system, we start by investigating the exciton energy shift in the case of a WS\(_2\) monolayer by measuring the reflection response while varying the temperature from 193 K to 513 K in an \(\text{N}_2\) atmosphere. Selected spectra are shown in Figure 6.19a, where a clear redshift is observed for increasing temperature. Furthermore, the exciton resonance is seen to broaden with increasing temperature as expected from the strong electron-phonon coupling and also observed experimentally [177].

In Section 6.2.1 the thermal deposition of SiO\(_2\) resulted in complete optical degradation of the MoS\(_2\). Figure 6.19b exemplifies the absence of this effect in the WS\(_2\). No significant degradation of the excitonic resonances is observed after successive heating steps, which we ascribe to the \(\text{N}_2\) atmosphere.

The extracted peak energies for each temperature is shown in Figure 6.19c. Fixing the average phonon energy to \(\langle \hbar \omega \rangle = 14.5\) meV [177], we find \(S = 1.7 \pm 0.2\), which is slightly lower than previously reported values both for WS\(_2\) and other TMDCs [177, 178]. We do, however, refine the linear dependence of the exciton energy with temperature also observed previously in this temperature range [174, 175, 177, 178].
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We now turn our attention to the evolution of the scattering spectrum of the coupled system represented by one of the nanodisks on monolayer WS₂ used in the previous experiments. A spectrum was obtained for temperatures from 233 K to 353 K in steps of 20 K. As the exciton energy changes with the temperature, we expect to see a shift in the spectral weight as we did in Figure 6.15b–c. Looking at Figure 6.20a, this is exactly what we observe when the temperature increases from 233 K to 353 K, where the ratio between the UPB and LPB is 1.98 and 1.67, respectively. As the monolayer system exhibits an FOM of only 1.09, raising the temperature too high would result in the system leaving the strong-coupling regime due to the increased exciton damping. However, even without crossing this threshold we can infer from the smaller magnitude of the dip in the scattering spectra that the system approaches the regime of induced transparency at higher temperatures.

Applying the same data analysis procedure as before yields the dispersion seen in Figure 6.20b, where we have redefined the detuning as \( \delta = E_{\text{ex}} - E_{\text{pl}} \), in order to keep the constituent with constant energy as the reference point. We clearly see that it is indeed possible to map out part of the dispersion in this manner, and we furthermore again find the linear dependence of the exciton energy with temperature. Extracting the exciton linewidth by fitting each scattering spectrum to the COM indicates that the damping varies from 17 meV to 30 meV in the temperature range. If the temperature was sufficiently increased, it could even be possible to dynamically change the state of the system in and out of the strong-coupling regime, as has also been done previously by changing the oscillator strength of a dye molecule with different gas flows [27].

Conclusion and outlook

In the previous we have seen the clear presence of the strong-coupling regime in the form of single-crystalline gold nanodisks on WS₂ mono- and multilayers. We
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Figure 6.20: (a) Scattering spectra of a single gold nanodisk strongly coupled to monolayer WS$_2$ at 233 K and 353 K with peak ratios of 1.98 and 1.67, respectively. This shows a shift in the spectral weight due to the change in the exciton energy. (b) Part of the dispersion relation constructed with a single nanodisk by sweeping the exciton energy. The temperature was varied between the two in (a) in steps of 20 K, and the dashed lines indicate the plasmon (horizontal) and exciton (sloped) energies. Note the new definition of $\delta = E_{ex} - E_{pl}$.

furthermore saw that it was possible in this system to increase the FOM by 50% due to the additional mode overlap between the plasmonic cavity and the excitonic material. This increased FOM of 1.64 $\pm$ 0.08 is, to the best of our knowledge, the highest reported to date in a coupled system comprised of an open plasmonic cavity and a TMDC. Additionally, we saw that it is also possible to control the exciton energy with temperature and the resulting effect on the scattering spectra.

Reaching the strong-coupling regime in this material platform is the first step towards future investigations into the rich physics contained within. However, as was shown in Paper B, and which was also evident from the spread of the measurement points in the obtained dispersion relations in Figure 6.15a and 6.18, there is a significant difference between the performance of individual particles. Exploring the strong-coupling regime using near-field techniques such as scattering near-field optical microscopy or EELS could give additional information on the involved mechanisms. Being able to consistently fabricate systems in the strong-coupling regime is crucial for future applications, as the approach taken here is less deterministic.

Recently, it was shown that collective nonlinearities can be enhanced when coupling excitons to a plasmonic cavity, such that it could be possible to observe non-classical light emission in these systems [179, 180]. These results indicate that in order for this to happen, the cooperativity of the system (here defined as $C' = 2\gamma^2 / \Gamma_{ex}\Gamma_{pl}$) should exceed $\sim$0.25. In our system we obtain $C' = 2.4$, which should at least theoretically allow for the generation of non-classical light. Furthermore, the interaction between individual TMDC layers can both be used to increase the coupling strength as seen here, but can also be used to create new exciton species altogether using different TMDC layers [11], with even more species appearing when rotating two layers with respect to each other [13–16]. These exciting results hold great promise for future possibilities of engineering the properties of the emitter states. These emitters also do not necessarily have to be hosted by the usual TMDCs discussed in this work. Indeed, with the many new materials predicted to be thermodynamically stable, but
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which have not yet been synthesised, there is a very real possibility that some may be discovered with even stronger light-matter interaction [2].
In conclusion, we have in this thesis investigated the optical properties of metallic nanostructures and different transition metal dichalcogenides (TMDCs), both alone and when coupled to each other in various configurations.

In the case of metallic nanostructures, we first investigated the influence on the optical properties of the surface states present on gold surfaces of the \{111\} crystal faces. This was done by using spherical gold nanoparticles and probing their interaction with these single-crystalline substrates in darkfield scattering spectra. No statistically significant change was found between a reference substrate in the form of polycrystalline, template-stripped gold as compared to the single-crystalline. This was ascribed to the small impact of the surface states, as predicted by finite-element method (FEM) calculations, when compared to other factors in the system such as the surface roughness of the substrates.

From this, we moved on to the concept of bandgap engineering in the TMDC WSe\(_2\). The structure under investigation was monolayer flakes of WSe\(_2\) sandwiched between two thick hBN flakes, the bottom of which was nanostructured in a hole antidot lattice. This lattice was varied both in size and pitch of the holes, which was grouped into a single parameter coined the hole fill fraction (HFF). By varying the dielectric environment, we showed that it was possible to gradually tune the emission energy of the strong A-exciton in WSe\(_2\) with increasing HFF. Reflection spectra of the same regions yielded no additional information due to the lack of a reliable reference measurement of the structured regions. However, comparison with literature hinted at a curious effect where there appeared to be either a red- or a blueshift of the resonance energy depending on the choice of molybdenum or tungsten chalcogenides.

Additionally, the coupling between semi-continuous gold films, so-called percolation films, and MoS\(_2\) was explored. In the case of emission strength of the A-exciton in MoS\(_2\), we saw a reduction for all deposited nominal gold thicknesses. Whether this was caused by insufficient cavity enhancement from the broad range of plasmonic resonances hosted by the percolation film compared to the nonradiative pathways introduced by the metal is unknown. However, reflection spectra revealed a significant decrease in signal intensity for all percolation film thicknesses as compared to the bare MoS\(_2\), where especially the film with a thickness of 3 nm showed
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a nearly 50% reduction. Although the origin of this reduction is unknown, the response of the system changes significantly when MoS$_2$ is present as compared to the percolation film directly on the substrate.

Finally, we have studied the coupling between single-crystalline, ultra-thin gold nanodisks coupled to WS$_2$ mono- and multilayers. By realising simultaneous spatial and spectral overlap of the localised surface plasmon in the nanodisk and the A-exciton in WS$_2$, we experimentally show the presence of the strong-coupling regime for the monolayer configuration in both scattering and reflection measurements. The latter is argued to be representative of the absorption properties of the coupled system, where the presence of mode splitting in absorption is indicative of strong coupling. We furthermore support these measurements with FEM calculations, where we obtain excellent agreement between experimental and numerical results. The system attained a figure of merit (FOM) $E_{Rabi}/\Gamma_{avg} = 1.09 \pm 0.08$ which is comparable to literature values for similar systems. This FOM was significantly increased by 50% to $1.64 \pm 0.08$, achieved by switching the excitonic material to seven-layer WS$_2$ and thereby obtaining a Rabi splitting of $E_{Rabi} = 175 \pm 9$ meV. The increase is ascribed to the enhanced mode overlap between the plasmonic mode and the excitons. These values represent the largest reported for an open plasmonic cavity coupled to a TMDC.

7.1 Outlook

As the work done in this thesis was fragmented between different projects, individual outlooks have been given after the results from each were presented. For this reason, the outlook will be comprised of suggested next steps for two of the projects, namely the bandgap engineering of 2D materials using nanostructured dielectrics, and the strong coupling between plasmons and excitons.

Starting with the bandgap engineering, it would be highly interesting to explore the apparent material dependence of the exciton energy shift in greater detail. Using e.g. both MoSe$_2$ and WSe$_2$, which feature similar excitonic energies, in the same dielectric environment would allow us to probe this effect. Understanding the microscopic origin of the behaviour of 2D materials is paramount to integrating them into devices.

In addition to this, studying the exciton centre-of-mass localisation would be of great fundamental interest, as this will improve our general understanding of these 2D excitonic systems. Being able to trap excitons in this manner could also lead to new applications in the form of exciton guiding, which is especially interesting in the case of trions, as these can be manipulated using an electric field.

Regarding the strongly coupled system, the work presented here and in Paper B was merely the platform to start exploring the realm of strong coupling. There are many attractive features in our system that warrants further investigations. As we have seen, it is possible to address the $K$- and $-K$-valleys in TMDCs independently using circularly polarised light. Due to the rotational symmetry of the nanodisks used, it could be possible to influence the coupling by using circularly polarised light, since the polariton retains a degree of excitonic character.

Furthermore, many results have been reported on the formation of new exciton species in Van der Waals-heterostructures, both stacked regularly and more recently by rotating the two layers with respect to each other [13–16]. An interesting route to
explore would be coupling to these new interlayer excitons, but also to try encapsulating the plasmonic cavity itself between layers of different TMDCs to investigate the simultaneous interaction between the localised plasmon and multiple different exciton species.


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(142) Sanchez-Mondragon, J. J.; Narozhnny, N. B.; Eberly, J. H. 
(143) Hsu, C. J. 
(144) Agarwal, G. S. 
(145) Kaluzny, Y.; Goy, P.; Gross, M.; Raimond, J. M.; Haroche, S. 
(146) Raizen, M. G.; Thompson, R. J.; Brecha, R. J.; Kimble, H. J.; Carmichael, H. J. 
(147) Bernardot, F.; Nussenzveig, P.; Brune, M.; Raimond, J. M.; Haroche, S. 
(148) Thompson, R. J.; Rempe, G.; Kimble, H. J. 
(149) Hood, C. J.; Chapman, M. S.; Lynn, T. W.; Kimble, H. J. 
(150) McKeever, J.; Boca, A.; Boozer, A. D.; Buck, J. R.; Kimble, H. J. 


A.1 Microscope

The set up is based on a Nikon Ti-U Inverted Microscope. This microscope allows for brightfield and darkfield transmission, and brightfield reflection measurements by default. However, it has been equipped with a special objective holder to allow for darkfield microscopy in reflection as well. Due to the increased height of this objective holder, the microscope stage has been lifted from its base position with two I-beams, but the specific configuration still only allows for the simultaneous use of at most two objectives: An overview objective (10x) and a measurement objective. A list of the available objectives can be seen in Table A.1.

<table>
<thead>
<tr>
<th>Objective</th>
<th>Mag</th>
<th>NA</th>
<th>WD [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFI TU Plan Fluor EPI</td>
<td>10x</td>
<td>0.30</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td>50x</td>
<td>0.80</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>100x</td>
<td>0.90</td>
<td>1.0</td>
</tr>
<tr>
<td>CFI TU Plan BD ELWD</td>
<td>50x</td>
<td>0.60</td>
<td>11.0</td>
</tr>
<tr>
<td>CFI S Plan Fluor ELWD*</td>
<td>60x</td>
<td>0.70</td>
<td>2.6-1.8</td>
</tr>
</tbody>
</table>

Table A.1: List of available objectives. NA: Numerical aperture; WD: Working distance. *: This objective has a correction collar for use with microscope slides of thicknesses 0.1-1.3 mm, hence the variable working distance.
Figure A.1: Top-down sketch of the microscope set up. DM: Dichroic mirror; P: polariser; λ/2: Half-wave plate; ND: Neutral density filter; SP: Shortpass filter; LP: Longpass filter; BS: Beamsplitter.

<table>
<thead>
<tr>
<th>Axes</th>
<th>Type</th>
<th>Range</th>
<th>Min. step size</th>
<th>Repeatability</th>
<th>Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>XY</td>
<td>Stepper</td>
<td>25 mm</td>
<td>95 nm</td>
<td>&lt;100 nm</td>
<td>2 mm/s</td>
</tr>
<tr>
<td>Z</td>
<td>Piezo</td>
<td>200 μm</td>
<td>0.4 nm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table A.2: Overview of the microscope stage’s specifications.
A.1.1 XYZ stage

The standard mechanical stage of the microscope has been replaced with an MCL-MOTNZ stage from Mad City Labs Inc., which features an XY-stage with an electromagnetic stepper motor and a Z-stage with a piezo motor. The stage’s specifications have been summarized in Table A.2. It is controlled through a LabVIEW interface supplied by Mad City Labs. Absolute positioning is not possible since the XY stage is not equipped with linear encoders, but the stepper motors do count the number of steps taken, and as such navigation relative to an origin is possible. The piezo in the Z-stage, on the other hand, has an absolute height value. An alternative to using the interface buttons is a gamepad, natively supported by the LabVIEW program, allowing for faster and easier control of the stage, which we currently use in the form of a Logitech F710 Wireless Gamepad.

The stage can also be custom programmed in either LabVIEW or another language as it runs on a C library, which means it is possible to perform more advanced movement patterns such as XY (or Z) maps and automated focus adjustments. Due to the high numerical aperture (NA) of the objectives and small minimum step size of the of the XY stepper’s movement, it is thus possible to do micro-mapping of a sample. The resolution is in part determined by the diffraction limited spot size of the objective. Taking as example photoluminescence measurements using the 100x objective with the highest NA yields a spot with radius 552 nm @ 407 nm. However, by hyper-sampling (i.e. measuring in smaller steps than the spot size) this resolution can in some cases be improved to e.g. detect material edges with higher spatial precision.

Since the XY movement is performed with stepper motors and there are no encoders on the stage to read absolute position, backlash of the stage has to be accounted for when doing a map. Backlash occurs due to the reversal of movement in the stepper motors and causes the stage not to move even though a command to move is given. Failing to account for backlash results in a map as shown in Figure A.2a, where the top line is an artefact induced from incorrect movement of the stepper motors. A way to solve this is presented by the stage itself, as it has a tendency to “catch up” to the movement lost from the backlash when moving far enough. Incorporating this leads to a map as shown in Figure A.2b, with the real-space image shown in Figure A.2c. The mapping pattern implementing the backlash correction can be seen in Figure A.2d, where the overshoot corrects for the errors otherwise induced by the backlash before moving on to the next column in the scan.

A description of the mapping algorithm in pseudocode can be seen in Algorithm 1.

Additionally, a custom mount has been made to fit a Linkam HFS600E-PB4 (−196 °C to 600 °C) stage with four electrical probes, which was used for the temperature measurements.

A.2 Illumination sources

The set up features four different illumination sources:

**Halogen lamp** with continuously tunable power from 0 W to 100 W. Spectra can be seen in Figure A.3a.

**Nikon Intensilight C-HGFI** fibre coupled lamp with discretely tunable power from 0 W to 130 W. A spectrum can be seen in Figure A.3b
A.2. Illumination sources

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figureA2}
\caption{Direct images exemplifying the effect of mapping (a) without and (b) with backlash correction. The real-space image directly from the CCD is seen in (c), and the movement of the stage using the implemented backlash correction is indicated in (d).}
\end{figure}

\begin{algorithm}
\caption{Mapping}
1: Initialise stage  \\
2: Initialise spectrometer  \\
3: Set up acquisition parameters  \\
4: Measure dark counts  \\
5: Set up map parameters \hspace{1cm} \triangleright \text{Size and number of grid points} (n_X, n_Y)  \\
6: Check if map fits within limits of stage movement  \\
7: \textbf{while} \ i \neq n_X \ \textbf{do}  \\
8: \hspace{1cm} \textbf{while} \ j \neq n_Y \ \textbf{do} \hspace{1cm} \triangleright \text{Move through } y \text{ grid points}  \\
9: \hspace{2cm} Acquire spectrum  \\
10: \hspace{2cm} Move stage in y  \\
11: \hspace{2cm} j \leftarrow j + 1  \\
12: \hspace{1cm} \textbf{end while}  \\
13: \hspace{1cm} Move stage in x  \\
14: \hspace{1cm} i \leftarrow i + 1  \\
15: \textbf{end while}
\end{algorithm}
Appendix A. Optical Set Up

Figure A.3: (a) Spectrum of the halogen lamp at powers from 40 W to 100 W. The cut-on at high energy is due to a 450 nm longpass filter. The sudden increase in signal at low energy is second-order diffraction from the grating. (b) Spectrum of the Nikon Intensilight lamp.

Figure A.4: Spectra of the (a) 407 nm and (b) 520 nm laser.

Two lasers 407 nm and 520 nm (3.05 and 2.38 eV) single-mode fibre coupled from Integrated Optics with continuously tunable output power from 0 W to 53 W and 0 W to 17 W, respectively. Spectra can be seen in Figure A.4a and A.4b.

The halogen lamp was used for all white-light spectroscopy in this thesis, and it has a typical black-body radiation profile with good signal strength throughout most of the visible region as shown in Figure A.3a. The spectra have been normalised for ease of comparison since the integrated intensity changes by a factor of $\sim 27$ from lowest to highest. Increasing the power also shifts the peak of the spectrum to higher energies, consistent with black-body radiation shifting to higher temperatures as the current through the halogen bulb’s filament is increased. The sharp cut-on at high energy is caused by a 450 nm longpass filter inserted at the spectrometer entrance, while the sharp increase in signal strength at low energy is second-order diffraction from the grating.
From the chemical synthesis of the nanodisks, organic residues are suspended in the solution. Before deposition these have to be removed, otherwise they can contaminate the sample and cover the flakes in place of the nanodisks. Even particles that seem to be on the flakes could potentially land on these residues instead, and as such an exhaustive study with e.g. atomic force microscopy (AFM) would be necessary to identify the useful particles. To remove the residues and prepare the solution for deposition, the following recipe was followed:

1. Take X µL of the initial solution and deposit in an Eppendorf tube.
2. Centrifuge the solution for 6 min with the RPM given in Table B.1.
3. Inspect the solution. If a thin line is visible at the bottom, the RPM used was fine (the line is the particles pushed to the bottom). If they lie in a circular pattern, repeat 2 with a higher RPM.
4. Remove excess liquid, which contains the impurities, without disturbing the nanoparticles.
5. Add X µL of DI water and repeat 2.
7. Add ~X/10 µL of DI water to obtain the final solution.

The amount of DI water added in the final step can be varied to obtain higher or lower concentration of particles, as required. Removing the excess contaminated liquid after each centrifugation step is tricky and requires a steady hand. However, this step is crucial to obtain a solution as free of contaminants as possible. An example of a deposition using a solution with contaminants can be seen in Figure B.1,

<table>
<thead>
<tr>
<th>Peak position [nm]</th>
<th>622</th>
<th>646</th>
<th>670</th>
<th>692</th>
<th>718</th>
<th>740</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPM</td>
<td>6400</td>
<td>6200</td>
<td>6000</td>
<td>5800</td>
<td>5600</td>
<td>5400</td>
</tr>
</tbody>
</table>

Table B.1: Rounds per minute (RPM) to use when centrifuging the nanodisk solution in order to remove contaminants.
Figure B.1: Darkfield image of deposited nanoparticles (red dots) with organic residues (blue "crystals"). Scale bar is 5 µm.

where the blue "crystals" are agglomerated organic residues with a surface coverage of ~50 %, while the red dots are the nanoparticles. Since the typical size of an exfoliated flake of WS$_2$ is only on the order of 10s of micrometers, there is precious little usable area. The interaction with the organic molecules can furthermore result in TMDC degradation during the deposition, and this should therefore be avoided at all costs.
Optical reconfiguration and polarization control in semi-continuous gold films close to the percolation threshold†

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Controlling and confining light by exciting plasmons in resonant metallic nanostructures is an essential aspect of many new emerging optical technologies. Here we explore the possibility of controllably reconfiguring the intrinsic optical properties of semi-continuous gold films, by inducing permanent morphological changes with a femtosecond (fs)-pulsed laser above a critical power. Optical transmission spectroscopy measurements show a correlation between the spectra of the morphologically modified films and the wavelength, polarization, and the intensity of the laser used for alteration. In order to understand the modifications induced by the laser writing, we explore the near-field properties of these films with electron energy-loss spectroscopy (EELS). A comparison between our experimental data and full-wave simulations on the exact film morphologies hints toward a restructuring of the intrinsic plasmonic eigenmodes of the metallic film by photothermal effects. We explain these optical changes with a simple model and demonstrate experimentally that laser writing can be used to controllably modify the optical properties of these semi-continuous films. These metal films offer an easy-to-fabricate and scalable platform for technological applications such as molecular sensing and ultra-dense data storage.

Introduction

The ability of metallic nanostructures to localize and enhance optical fields down to the nanoscale via collective electron excitations (plasmons) has been the subject of intense study in the recent decades. Many promising applications arise from the careful engineering of nanostructures to tune their optical properties. This allows sub-diffraction light focusing for spectroscopy and sensing applications like surface-enhanced Raman scattering (SERS),2 enhancing light-matter interaction with new 2D materials,3,4 and quantum information processing technologies.5–7 Another application recently gaining in popularity is the tuning of a surface’s spectral reflectivity by plasmonic nanostructures to produce colour images8 with ultra-dense information storage.9–11 However, due to the nanometre size scales needed these structures often require elaborate fabrication methods such as electron-beam lithography (EBL) or focused ion beam (FIB) milling.12 EBL allows for precise and reproducible definition of nanostructures but at the cost of time consuming process steps to produce a mask pattern in a polymer resist.13 Additionally, in most state of the art lithography systems the spatial resolution is still limited to about 10 nm.14 FIB offers an alternative method for high-resolution and mask-less fabrication, but still requires long pattern writing times, and also comes with the potential problem of contaminating the structure materials with the milling ions.14

Self-assembled and self-similar metallic structures where high levels of field enhancement are hosted by the naturally occurring sub-nanometre sized gaps or protrusions, are thus of great interest as they offer an alternative source of strong field localization and enhancement. Typically these structures also have fast and scalable (bottom-up) fabrication methods with few processing steps.15–17 While these types of structures promise scalable and easily fabricated nanostructures, their specific optical properties are however limited within the scope of their assembly methods. One way to expand the range of achievable excitations is of course to influence the assembly

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process during fabrication, but another way is to alter metallic and dielectric nanostructures post-assembly via controlled photothermal reshaping. One such system, that we study here, is thin gold films near the percolation threshold subjected to morphological modifications by pulsed laser illumination. The nanostructured morphology of percolation metal films arises from the Volmer-Weber process of metal growth on amorphous dielectric substrates. During the deposition process the metal atoms have a mutually strong interaction, while interacting less with the substrate. This leads to the formation of isolated clusters that tend to grow in the substrate plane during deposition, eventually reaching a percolation threshold where they merge to form a connected system. Further metal deposition will then serve to close up any remaining gaps in the film morphology, and eventually the system will transition into a metal on metal growth process. Depending on the deposition parameters and substrate used, it is possible to routinely fabricate large-scale areas of such metal structures where the smallest feature sizes can be at the sub-nanometre scale.

These films also hold interesting non-linear optical properties with prospects for white-light generation with modest pump powers. However, the optical properties of these films remain to be fully investigated with dedicated spectroscopic methods. The small feature sizes of these metal films present a significant challenge for experimental exploration with conventional near-field optics. For scattering scanning near-field optical microscopes (s-SNOMs) the spatial resolution limit of the setup will still be defined by the cantilever tip size, which in the most state of the art devices is still in the order of a few nanometres. Despite being an exceptionally high spatial resolution for photon-based characterization, the limited spatial resolution of the tip does not allow to explore the optical properties of ultra-small plasmonic gaps with dimensions on the single nanometre scale and below. Furthermore, s-SNOM techniques are usually spectrally limited to a single or a small set of energies which is detrimental to fully characterize the plasmonic eigenmodes of these complex structures. Electron-based spectroscopic techniques such as energy-filtered electron energy-loss spectroscopy in monochromated transmission electron microscopes (TEMs) offers an attractive alternative to access the optical properties of nano-metre and sub-nanometre sized plasmonic structures.

Indeed, the exceptional sub-nanometre spatial resolution and the broadband excitation spectrum of the electron beam has recently been used to spatially map the intrinsic plasmonic eigenmodes in self-similar pristine silver films. This method permits to identify unambiguously plasmonic hot spots that are not related to the morphology of the films in a simple way, as predicted theoretically. Here we explore novel aspects of the optical reconfiguration of the plasmon excitations in gold films near the percolation threshold. After illumination with a fs-pulsed laser above a critical power, it is possible to induce permanent morphological modifications in the films. For clarity we will refer to this process by laser writing in the rest of the text. These morphology changes allow for controlled changes to the film’s optical properties. Using optical transmission spectroscopy, we demonstrate how it is possible to inscribe polarized and wavelength selective field enhancement into these otherwise broadly resonant films with laser writing. We explain the morphology changes of the films from laser writing by photothermal reshaping of the metal nanoparticles in resonance with the excitation wavelength. We show that this process depends intrinsically on the degree of film percolation, illumination power, polarization, and wavelength of the laser. Our explanation includes three different processes: particle spherification for elongated nanoparticles, dimer decoupling for large plasmonic gaps, and dimer welding/particle fusion for small gaps. We use hyperspectral imaging with nanometre resolution to show statistically the effect of morphological changes on the distribution of plasmonic modes in the near-field. By utilizing full-wave simulations of our explored morphologies, we highlight that the polarization dependence in the inscribed films originates from resonant elongated particles that have formed during the photothermal processes. Despite the complexity of the optical properties in these percolation films, we show that the far-field optical properties can be modified controllably through laser writing.

**Results and discussion**

**Morphology changes and induced optical anisotropy**

We have fabricated 3 samples of thin gold films on 18 nm thick SiO₂ TEM membranes (see methods). The films are of nominal thicknesses 5, 6, and 7 nm. After fabrication, a series of areas on the gold films are illuminated by scanning a fs-pulsed laser at various powers across the films, Fig. 1a (see Methods). If the illumination is performed above a critical level of laser power, permanent morphological changes will be induced in the films. The degree and nature of this morphology reconfiguration can be controlled based on the scan parameters used, but principally depend on the laser power or wavelength used. Fig. 1b shows scanning transmission electron microscope (STEM) dark-field images of the intrinsic film morphologies, and examples of the effect of laser writing (a more detailed morphology study is available in ESI Fig. 1 and Discussion†).

In Fig. 1b we observe that the reconfiguration of the gold films is remarkably different for percolated (7 nm) and unpercolated (5 and 6 nm) samples. Indeed, high powers in the writing laser will generate more isolated nanoparticles in gold films with thicknesses below the percolation threshold. This is in stark contrast to the percolated metal film where the film is already an inter-connected network of clusters, and it remains a network of connected gold clusters even for much larger laser powers.

To understand how the morphology changes are linked to changes in the plasmonic resonances in the intrinsic film, we present a simple toy model of resonant elongated particles that have their aspect ratios altered while maintaining their initial volume (see Methods). We can imagine that three
Different scenarios will occur during the photothermal reshaping: Particle shortening/spherification, particle decoupling/gap widening, and particle fusion/welding. In Fig. 1c we highlight how shortening a particle while adding the ‘lost’ volume to either its height or width will result in a blueshift of the particle’s longitudinal mode. This change in aspect ratios will correspond to the general contraction of a metal cluster into a more spherical shape due to the surface tension in the molten metal trying to minimize the particle’s surface energy. In Fig. 1d we show how this kind of particle contraction (lost volume in length added to height) of two coupled particles will again result in a blueshift of the system’s longitudinal mode from increasing the gap distance between them. When the two particles are sufficiently contracted, their coupling will also be

Fig. 1 Optical reconfiguration of thin gold films. (a) Schematic overview of the laser writing process used to alter sample morphology. (b) STEM dark-field images of intrinsic film morphologies and laser written morphologies. All images at same scale, scale bar is 150 nm. (c) Simulations of the blueshift of longitudinal resonance energy for a particle being shortened, and then either widened or increased in height to preserve particle volume. (d) Simulation results of the blueshift from opening of a gap between two plasmonic particles from shortening the particles. (e) Simulation of how closing of a plasmonic gap and merging the two particles (welding) causes a redshift in resonance energy. (f–g) Transmission dark-field images of stripes written in the gold films with (f) different laser powers with a 740 nm wavelength, and (g) with different laser wavelengths. White arrows on the images indicates the polarization of laser writing, black arrows on left show the polarization used for illumination when recording the image. Scale bar is 7.5 μm.
broken and they will start resonating like two individual particles. This kind of morphology change will correspond to how plasmonically coupled clusters that are too far apart for particle welding/fusion will become decoupled. Finally in Fig. 1e we have the scenario of two metal clusters that are close enough to each other to fuse under laser writing. We here simulate the fusion process by progressively moving the two elongated particles closer to each other, and when they start to overlap (gap size of 0) the overlapping volume gets added to the resulting single particle’s height. Both in terms of closing the gap distance and merging the two particles into one, a general redshift of the initial resonance is observed, with a strong shift at the merging point. After merging, the combined particle exhibits single particle behaviour (see Fig. 1c).

The effect of the laser writing on the gold films and its morphological changes can be observed with a microscope at low magnification, as shown in Fig. 1f and g. From Fig. 1f and g we see a clear difference between the illuminated and the unilluminated regions of the gold films from the distinctive colours that emerge from the morphological changes in the film. Interestingly, from Fig. 1f and g, we also see that the laser writing has left behind a polarization dependence in the films’ optical properties, correlated with the polarization of the laser used to perform the writing, as a redder hue becomes visible when the polarization of the illumination in the microscope (black arrow) is aligned with the one used in the laser writing (white arrow).

Optical far-field properties of optical reconfigured gold films

To investigate the emergent red colour from laser writing in greater detail, we perform optical spectroscopy on our samples with an inverted microscope connected to a state of the art spectrometer (see Methods). From the bright-field transmission spectra of Fig. 2 (full data available in ESI Fig. 2†), when aligning the polarization of the light source in the transmission experiment parallel with the polarization of the laser used for the writing, we see a sharp decrease in transmission for photon energies in the range of 1.8–2.0 eV. When turning the polarization of the light source in our microscope to the perpendicular direction of the laser writing, this feature is strongly suppressed. On Fig. 2c we show for the 5 nm sample that the position of this feature is also dependent on the wavelength used for the writing process, with longer wavelengths also producing a feature deeper in the red part of the spectrum. For the 7 nm (and 6 nm) sample this feature is less pronounced for the lower powers used, but it still becomes apparent for sufficiently high writing powers. This can be understood from comparing the morphologies in Fig. 1b, as the thicker gold films seem generally less perturbed by the laser writing. We explain this from the fact that the 6 and 7 nm films appear to be close to and above the percolation threshold, respectively. As such, higher levels of laser power is needed to fully separate the particles as heat will be more efficiently conducted away from its injection point in a connected system.47,48 Another observed trend is that the central position of the transmission feature tends to blueshift for increasing levels of laser power used for the writing. We attribute this to two effects. First, the individual particles become shortened for the higher writing powers, due to increasing spherification of the gold at higher temperatures, and secondly due to the likewise increasing thickness of the gold particles as the volume of gold that was previously covering the flat surface now accumulates into thicker particles (when we assume only minimal gold evaporation).

Statistical analysis of EELS intensity distributions

We have shown that laser-induced reshaping of the metal films has a strong effect on their optical far-field properties. In order to investigate the plasmonic properties of the individual particle clusters and gaps, we recorded high resolution EELS maps of the samples. Due to the highly random nature of the film morphologies, the specific detailed distribution of the

Fig. 2 Optical anisotropy. Polarized bright-field transmission spectra of the (a) 5 nm, (b) 7 nm films from regions illuminated with different laser powers, and (c) for illumination with different photon energies on the 5 nm sample. Vertical black lines indicate the photon energy of the laser used. The white-light source used to illuminate the samples in the measurements was polarized parallel or perpendicular to the polarization of the laser used for writing.
electric fields associated with the plasmon resonances is difficult to reproduce, making qualitative comparisons between samples difficult (example EELS maps are available in Fig. 3a). Secondly, comparisons between large sets of EELS maps for such random geometries can become very overwhelming to interpret. But, due to the self-similar and isotropic nature of the films, a quantitative statistical analysis of sufficiently large regions of the films can provide a reproducible and comparable probability distribution function (PDF) of the EELS intensity of a specific film morphology. Furthermore, the total shape of the PDF informs us on the degree of coupling between the plasmonic eigenmodes in the semi-continuous film. A Gaussian shape corresponds to plasmonic excitations coupled throughout the metal film, while a more power-law shape (see lines in Fig. 3e and f) corresponds to isolated plasmonic excitations.31

In order to construct PDFs of our EELS intensities, we take advantage of the methods of previous theoretical and experimental works on self-similar and fractal structures.31,49,50 In short, for each spectral image we can extract the resonance energy and EELS intensity of the measured plasmons. By then binning the found intensities we form a distribution of intensities in the spectral image (i.e. a histogram). For each intensity value, this PDF then gives us the probability of finding this EELS intensity in the image (see methods for more details). The EELS intensity gives the probability of an electron losing a certain amount of energy along its trajectory through the sample, and it is proportional to the integral of the electric field induced in the sample along this trajectory by the electron.44 As such, the EELS intensity is not itself a direct measure of the plasmonic electric field amplitude, but the two are strongly related.44,51–53 We use this to justify the comparison of EELS intensity to previous measurements and calculations of the near-field intensities of semi-continuous metal films.

To extract the plasmon resonant energies and peak intensities from our background-corrected spectral images, we perform an iterative series of Gaussian fits on the individual spectra. First a set of energy ranges of interest are determined from taking an average of the full spectral image, and within these energy ranges individual Gaussian functions are fitted to a smoothing spline constructed from the data. The parameters of these fits are then used for initial guesses to fit a sum of Gaussian functions that are fitted to the full range of the individual spectra’s datasets (see methods for more details). An example of these sequential fits can be seen in Fig. 3b. From the extracted peak central energies we can construct histograms of how the resonances are concentrated in terms of energy, and from the found peak intensities we can construct distribution functions of the EELS intensities in terms of their spectral position (Fig. 3c–f, and ESI Fig. 3–5†). For all of the films we see that prior to optical reconfiguration the central

![Fig. 3 Plasmonic resonance distribution. (a) Integrated EEL spectra overlaid on STEM dark-field images for 5 and 7 nm morphologies. Scale bar is 75 nm. (b) Example of an EEL spectrum and Gaussian fits used to extract peak central positions and energies, taken from the white dot in (a). Normalized histograms of identified central energies of plasmon resonances in the (c) 5 nm and (d) 7 nm films before and after laser writing. Constructed PDFs of the EELS intensity distributions for the intrinsic and reconfigured (e) 5 nm and (f) 7 nm samples. Straight lines added as a guide to the eye.](image-url)
energies of the detected plasmon resonances form a wide continuum with a slight peak in the distribution around 2.1–2.2 eV. The position of this peak in the distribution seems to red-shift slightly for increasing film thickness. The constructed PDFs for the intrinsic films also show that the near-infrared and red part of the spectrum (1.3–1.8 eV) contributes with higher relative EELS intensities (seen from the total width of the PDFs), in agreement with prior experiments and the scaling theory for semi-continuous metal films predicting higher field enhancement for longer wavelengths.\textsuperscript{31,54,55}

As the samples get subjected to high laser powers, we see a dramatic redistribution of the resonance energies, as well as the intensity distributions (results for the full range of powers on the three film samples are available in ESI Fig. 3–5†). The effect is especially pronounced for the 5 nm sample, Fig. 3c and e, where increasing levels of power of laser writing gradually reshapes the PDFs from the normal distribution expected for these kinds of films, towards a scaling power-law of isolated dipoles.\textsuperscript{31,49} We explain this from the morphology images in Fig. 1b and our toy model in Fig. 1c–e. For the high laser powers we see the inter-particle gaps increase significantly, and the resulting morphology consists mainly of isolated particles. As a result, the inter-particle coupling present in the intrinsic films has been lifted. This isolating and the reshaping into thicker and more spherical particles also explains why we generally see a strong blueshifting in the resonance energies in Fig. 3c. For the 7 nm sample we see a distinctly different morphology and resonance behaviour, compared to the 5 nm sample. For all levels of laser writing power the 7 nm sample remains a connected structure forming large networked clusters, where the small gaps that previously dominated the morphology either have fused or opened fully. The removal of these small features and their replacement by large connected clusters can help us to understand why the laser written film seems to have a large increase in red and near-infrared modes in Fig. 1d. From the fact that the structures also never become truly isolated, we can understand why the EELS intensity distributions for the laser written parts do not deviate as dramatically in their shape from the intrinsic PDFs, as in the 5 nm case. Interestingly, we are able to see a large increase in the relative EELS intensities from the \(\sim 1.9\) eV part of the spectrum in the laser written parts of the 5 nm film, when compared with the intrinsic films. This increase in intensity also seems to become larger for increasing powers of laser writing, and it is worth noting that the energy corresponds to the reduction in far-field optical transmission observed for the parallel polarization for the 5 nm sample in Fig. 2a.

**Polarization dependence**

In order to qualitatively investigate the polarization dependence of the extinction features seen in the transmission spectra of Fig. 2, we have constructed EELS maps for the 5 nm film samples by integrating the EEL spectra in the 1.8–2.0 eV energy range, as seen in Fig. 4 (full energy ranges are available in ESI Fig. 7–10†). From these maps several elongated particles appear to host dipole-like plasmon resonances, that are predominantly aligned with the direction of the polarization of the laser used to induce the optical reconfiguration. To verify if these particles are dominated by a dipolar response in this energy range, we performed finite-element simulations of plane wave excitations with two orthogonal polarizations on
the same film morphologies (see Methods). A comparison between the simulated field distributions and the measured EELS intensities can be seen in Fig. 5. Because the plane wave simulations allow us to make comparisons to the two excitation polarizations individually, we can now see how the measured plasmon resonances from the EELS data are decoupled in terms of polarization. With this we show that the suspected elongated particles are in fact behaving like strongly polarized nanorods with resonances in the same energy range as the features measured in the transmission experiments. A one-to-one comparison of EELS and plane-waves is usually difficult due to the inherent differences of the excitation sources.37,56,57 The electron beam in EELS is able to excite plasmon modes that are normally inaccessible with optical fields,58 and is also able to excite all different polarizations simultaneously.44,51 However, here we are only interested in identifying the bright modes around 1.9 eV that are optically active in our transmission measurements. We expect from this comparison to identify the polarization dependence of the plasmonic modes in the reshaped films (Fig. 2). Similar comparison between hyperspectral imaging and finite-difference simulations have been used to identify the polarization dependence of the optical response of resonant wedge-plasmons59 and of toroidal modes in heptamer and hexamer nanocavities.60

Conclusions

In summary, we have characterized the morphological and plasmonic restructuring of semi-continuous gold films of nominal thicknesses 5, 6, and 7 nm when subjected to fs-laser pulses of different powers (Fig. 1 and ESI Fig. 1†). This kind of optical reconfiguration becomes apparent in the far-field properties of the films, as a resonant feature is seen in the transmission spectra from the laser written areas of the films. When the samples are illuminated with a polarized light source that is aligned to the polarization of the laser used for the optical reconfiguration, a strong decrease in transmission is observed. Furthermore, the spectral position of this transmission feature can be controlled by varying the laser wavelength and power when performing the optical reconfiguration (Fig. 2). By measuring EELS maps from selected regions of the altered and intrinsic parts of the samples, we have constructed histograms of the central energies of the plasmon resonances present in the films, as well as PDFs of the EELS intensity distributions for different resonance energies (Fig. 3 and ESI Fig. 2–4†). From these we conclude that generally the resonances at longer wavelengths have higher EELS intensities in the intrinsic films, while in the altered films we observe a redistribution of the resonances that contribute to the largest EELS intensities, in qualitative agreement to our toy model. The intensities in reconfigured films are also generally higher overall, when compared to the intrinsic films. Finally, we have investigated the origin of the polarization dependence of the features observed in the transmission experiments, by plotting EELS intensity maps of energies related to the measured decrease in transmissions (Fig. 4). We have performed finite-element simulations to reconstruct the electric field distributions in our sample morphologies from polarized far-field excitation. We compare these to the measured EELS intensities to confirm that the resonant particles formed after laser
writing are responsible for the polarization dependence of the measured transmission spectra (Fig. 5).

These types of metallic films have previously been demonstrated to function as SERS substrates. We show here that it is possible to convert the broad ensemble of different plasmonic resonances found in these films into a more narrow band of resonances, making the films more selectively resonant for a specific wavelength and polarization of light. This could potentially be used to further increase the enhancement factor from such films in SERS applications, by tuning and enhancing the resonances towards the wavelength and polarization of the laser used in the Raman experiment. New sensing applications could also harness the potential of these kinds of metal films.

Finally, we have shown that by using a different laser wavelength or power when performing the optical reconfiguration it is possible to tune the wavelength of the resulting resonant particles created in the film. This could be useful for plasmonic colour printing by laser writing, as it would be possible to inscribe pixels of different colours into the films by using different wavelengths and powers, constructing a colour image that would be visible clearly when viewing the film through a correctly aligned polarizer. The spatial resolution of this writing method will at least be diffraction limited, as observed in our previous work (see Fig. 4 in ref. 28). Although nonlinear effects could increase this resolution, as seen in multiphoton absorption lithography. This could be the scope of future investigations. Recent experiments have already been performed demonstrating laser writing, but rely on using specifically fabricated substrate structures. The ease with which these metal films can be fabricated, even at very large-scale areas, could offer an alternative low-cost substrate structure for emerging plasmonic colour printing technologies, as well as applications in ultra-dense data storage media.

Experimental

Sample fabrication

Thin gold films of 5, 6, and 7 nm nominal thicknesses were deposited onto 18 nm thick SiO2 TEM membranes from Ted Pella, Inc. using an electron beam deposition system. The gold was deposited with a constant rate of 2 Å s⁻¹, with the total deposition time defining the thickness of the final film. Chamber pressure was maintained at ~10⁻⁵ mbar and deposition was on room temperature substrates.

Optical reconfiguration

The laser writing is performed with a two-photon photoluminescence (TPL) setup, consisting of a scanning optical microscope in reflection geometry built based on a commercial microscope with a computer-controlled translation stage. The linearly polarized light beam from a mode-locked pulsed (pulse duration ~200 fs, repetition rate ~80 MHz) Ti-Sapphire laser (wavelength λ = 730–860 nm, δλ ~ 10 nm, average power ~300 mW) is used to locally restructure the gold film at the fundamental harmonic (FH) frequency. After passing an optical isolator (to suppress back-reflection), half-wave plate, polarizer, red colour filter and wavelength selective beam splitter, the laser beam is focused on the sample surface at normal incidence with a Mitutoyo infinity-corrected long working distance objective (100×, NA = 0.70). The FH resolution at full-width-half-maximum is ~0.75 μm. The half-wave plate and polarizer allows accurate adjustment of the incident power. The laser writing was done with the following scan parameters: Integration time (at one point) of 50 ms, speed of scanning (between the measurement points) of 20 μm s⁻¹, and scanning step size of 350 nm. The incident power was within the range 0.5–2.0 mW. Unless stated otherwise, the excitation wavelength was fixed at 740 nm. We should mention that with this laser power, morphology changes could only be induced in the pulsing regime of the laser.

Optical spectroscopy

Bright-field transmission spectra were recorded from the intrinsic and laser written regions of the samples on the TEM membranes. A custom spectroscopy setup built from a Nikon Eclipse Ti-U Inverted microscope was used. The system is fitted with a halogen white-light source with peak emission at 675 nm. The light is collected by a CFI S Plan Fluor ELWD objective from Nikon (60×, NA = 0.70), and the spectra are recorded using a Shamrock 303i Spectrometer equipped with a Newton 970 EMCCD. A LPVISE200-A visible linear polarizer from Thorlabs is placed between the light source and sample stage, allowing for polarized illumination. Spectra are collected for polarizations perpendicular and parallel to the optically induced changes in the gold films. The transmission spectra are corrected for the spectral profile of the halogen lamp by recording a reference spectrum through a similar glass slide as the membranes are mounted on, for both polarizer positions. After dividing the intensities point by point with the reference, the final spectrum is obtained by averaging over the individual laser modified areas (~20 pixels on the CCD) and normalizing with the maximum value for comparison.

STEM and EELS measurements

The EELS measurements were performed with a FEI Titan TEM equipped with a monochromator and a probe aberration corrector. The microscope was operated in STEM mode at an acceleration voltage of 120 kV, with a probe diameter of 0.5 nm and with zero-loss peak (ZLP) full-width-half-maximums of ~0.2 eV. For spectral images, 500 × 500 nm² areas were scanned with 5–8 nm step sizes, using larger step sizes for the films modified by high laser powers. Before imaging, the samples were cleaned in an O₂-plasma for 45 s.

From the width of the ZLP, its central position is determined and the energy scale of the spectra is shifted to zero for this position. The spectra are then normalized by integrating the background signal found in the higher energies of the spectrum. After normalization the ZLP is subtracted by performing a series of power law fits, and the fit producing the minimum residual is picked. The full background corrected spectral image is averaged together, and a sum of Gaussian
functions are fitted to the now emerging ‘primary modes’ of the image, *i.e.* the modes so sufficiently common or intense that they contribute overwhelmingly to the total average of the spectral image. A smoothing spline is then constructed for each individual spectra’s data. These smoothing splines are then segmented within the full-width-half-maximum of the Gaussian functions fitted to the ‘primary modes’, and within each of these data segments a Gaussian function is fitted. The quality of these individual fits are then evaluated to determine if a peak is present in this energy range of the spectrum or not. From each segment of the spectrum, we now get the information if a peak is present, and if so, what its amplitude and central position is. Using these values for initial guesses, a sum of Gaussian functions are then fitted to the full range of the spectrum’s dataset and the plasmon resonance energies and EELS intensities are extracted from these fits.

**Statistical analysis**

Using the central position of the Gaussian fits described above, a histogram can be constructed of identified central energies, with bin sizes of 0.01 eV, matching the energy resolution of the TEM’s detector. The PDFs of discretized windows of the energy range are constructed from the corresponding amplitudes of the Gaussian fits with central energies in those windows. Each energy window is 0.10 eV wide, and to construct the PDF the fitted amplitudes are binned into 30 equally wide bins of intensities. We have estimated a base level intensity as the median of the 50 lowest identified amplitudes from each of the spectral images for each sample. All the identified intensities for each energy window are then normalized with respect to this base level intensity to be represented in terms of a relative EELS intensity.

**Simulations**

Full-wave 3D simulations of the gold structures were carried out using the finite-element software package COMSOL Multiphysics (v5.1). The simulation domain was truncated with perfectly matched layers from all sides. The system was solved in a scattered wave formulation, with analytical solution for three layer system (air–glass–air) as the background field. A custom Python script was used, which generated the simulation geometry from the outlines that were extracted from the binaries of STEM dark-field images (see ESI Methods†). The particles were represented as straight prisms in the 3D geometry. The relative thicknesses, $t_i$, of the gold films have been calculated by $t_i = \log(I_{tot}/I_{2LP})$, where $I_{2LP}$ is the integral of the ZLP in the EEL spectrum, and $I_{tot}$ is the total integral of the EEL spectrum, ranging from 0–17 eV. Calculating this for each pixel in our spectral images, and performing a plane background correction to this, provided the relative height map for the samples. By averaging the height map values inside the particle contours, the relative heights of the particles were obtained. The tallest particles were set to a height of 28 nm, as this provides the best correlation to the EELS measurements. An example of obtained particle contours and their relative heights are shown in ESI Fig. 6.†

Simulations for Fig. 1c–e are based on a similar setup. One or two nanorods are placed on the glass membrane. Calculations for Fig. 1c are done with a single nanorod that is composed of a rectangular prism (width $w$, height $h$, length $l$) with semi-cylindrical caps (radius $w/2$) at both ends. A series of calculations was done, for various lengths of the particle. For each particle size an absorption spectrum was calculated and the corresponding resonance peak was found. The particle size was varied to model the melting process, but the particle volume ($V = hwl + 2\pi w^2/4$) was kept constant either by scaling the particle height ($h$) or particle width ($w$).

For Fig. 1d we simulated two nanorods, with fixed centre positions. Consequently, as the particle length was reduced the gap between the nanorods increased. Particle height was scaled to keep the volume of the particles constant as they decreased in length.

For Fig. 1e the particle length was kept constant but the distance between the two particles varied. For positive gap sizes the particle shape stayed constant, but for negative gap sizes (particle overlap) the particle height was increased to keep the volume of the merged particle equal to the volume of the two initial particles.

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**References**

Supplementary Information: Optical reconfiguration and polarization control in semi-continuous gold films close to the percolation threshold

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Supplementary Figure 1: Sample morphologies. Area vs. perimeter plots of particles in HAADF images of the (a) 5 nm, and (b) 6 nm films before and after optical illumination. Slopes of linear fits are indicated and the full black lines are for perfectly separated circular particles. Because the 7 nm film consists of a fully interconnected film with only gaps, a similar plot cannot be produced for it. HAADF images of gold films, (c) 5 nm, (d) 6 nm, (e) 7 nm. The numbers in the lower left corners of the images indicate found filling fractions of gold, numbers in the upper left corners are the laser power used for illumination, and for all samples a wavelength of 740 nm was used. All images at same scale, the scale bar is 150 nm.
Supplementary Figure 2: Transmission spectra. Full transmission data from the (a) 5 nm, (b) 6 nm, and (c) 7 nm samples. The light source was either polarized parallel or perpendicular to the polarization of the laser used for the reconfiguration.
Supplementary Figure 3: Mode distribution 5 nm. (a) Normalized histograms of identified central energies of plasmonic peaks from the full spectral image of the 5 nm film with different powers of optical illumination. (b) PDFs of relative EELS intensities. The dataset of (a) has been discretized into several 0.1 eV windows, and PDFs have been constructed from the intensities of peaks in these ranges.
Supplementary Figure 4: Mode distribution 6 nm. (a) Normalized histograms of identified central energies of plasmonic peaks from the full spectral image of the 6 nm film with different powers of optical illumination. (b) PDFs of relative EELS intensities. The dataset of (a) has been discretized into several 0.1 eV windows, and PDFs have been constructed from the intensities of peaks in these ranges.
Supplementary Figure 5: Mode distribution 7 nm. (a) Normalized histograms of identified central energies of plasmonic peaks from the full spectral image of the 7 nm film with different powers of optical illumination. (b) PDFs of relative EELS intensities. The dataset of (a) has been discretized into several 0.1 eV windows, and PDFs have been constructed from the intensities of peaks in these ranges.
Supplementary Figure 6: Simulation geometries. Overview of the process to generate the thin film geometries used in simulations. The dark-field STEM images are converted to binaries to recover the particle outlines, and the EELS data is integrated in order to construct relative thickness maps of the samples. Using the thickness map and the particle outlines, an average thickness of each gold particle is found and the sample geometry can be constructed.
Supplementary Figure 7: EELS maps, y-polarized sample. Integrated EELS data in several energy ranges super imposed on STEM-images for initial 5 nm sample illuminated with 1.5 mW with y-polarization.

Supplementary Figure 8: Simulated fields. y-polarized sample. Norm of simulated electric field z-components for extracted geometries superimposed on the STEM-images of the sample.
Supplementary Figure 9: EELS maps, x-polarized sample. Integrated EELS data in several energy ranges super imposed on STEM-images for initial 5 nm sample illuminated with 1.5 mW with x-polarization.

Supplementary Figure 10: Simulated fields. x-polarized sample. Norm of simulated electric field z-components for extracted geometries superimposed on the STEM-images of the sample.
Supplementary discussion

Sample morphologies. The illuminated and intrinsic regions of the films are investigated with a scanning transmission electron microscope (STEM), where we image the films with the high angle annular dark-field (HAADF) detector. From our HAADF images we are able to characterize the morphologies of these films and their filling fractions (see supplementary methods), as well as how these evolve with the different powers used for inducing optical damage to the samples. From (Fig. 1a,b) we get an indication of the fractal nature of the gold particles in the film morphologies across different size scales. If self-similarity is preserved for increasing particle sizes, then the perimeter per area ratio is also preserved and the points will fall along a linear expression. The slope of this expression will give us a quantitative measure of the tortuosity of the system, and we can extract the slope via a linear regression. A system of perfectly separated disks will have a slope of 0.5 perimeter per area, while for increasingly tortuous systems the slope will increase as the particle perimeter grows faster than the particle area. From the 5 and 6 nm films we see that we get two regimes of particle shapes. The smallest particles are falling almost perfectly on the calculated line for circular particles, while above a certain size the particles start to form serpentine structures. We find generally that tortuosity is preserved for the optically reconfigured samples, only decreasing for higher power laser writing. We observe a general trend toward larger circular particles for increasing laser powers. We explain this from the morphologies displayed in Fig. 1.c,d,e, where we see a larger fraction of particles being affected by the laser at higher powers. The surface tension in the molten gold particles, and the high wetting angle of gold on silica, will tend toward spherizing the particles to minimize their surface energies\(^1,2\). Since the 7 nm sample consists of only one connected cluster the same type of analysis has not been possible.

Supplementary Methods

Sample morphology analysis. 8-bit greyscale HAADF STEM images of a 986 × 986 nm\(^2\) sample area with 512 × 512 pixel resolution were used for the image analysis. A histogram of the greyscale distribution was constructed for each image, and the minimum between the majority dark and majority light parts of the image was used as a threshold for converting the images to black and white binaries. A median filter with a 4 × 4 pixel neighbourhood was applied to the binary images to smoothen the particle outlines, and particles touching the borders of the images were excluded from the analysis. The surface areas and perimeters of the particles were then determined using the particle analysis toolbox in imageJ. The distance of the data points to the theoretical expression for perfectly circular particles was calculated for each data point, and the points closest to the circle line were excluded from the linear fits to find the loglog-slope of the datasets.

Supplementary References

Single-crystalline gold nanodisks on WS$_2$ mono- and multilayers for strong coupling at room temperature

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Abstract

Engineering light–matter interactions up to the strong–coupling regime at room temperature is one of the cornerstones of modern nanophotonics. Achieving this goal could enable new platforms for potential applications such as quantum information processing, quantum light sources, and even quantum metrology. Layered materials like transition metal dichalcogenides (TMDCs), and in particular tungsten disulfide (WS$_2$), possess strong dipole moments which are comparable to semiconductor-based quantum dots, but the former also exhibit large exciton binding energies, thereby making TMDCs suitable candidates for exploring light–matter interactions at ambient conditions. Furthermore, the combination of TMDCs with plasmonic nanocavities—which tightly confine light down to nanometer scales—has recently emerged as a suitable platform for achieving strong coupling between plasmons and excitons at room temperature. Here, we use ultra-thin single-crystalline gold nanodisks featuring large in-plane electric dipole moments aligned with the exciton’s dipole moments in monolayer WS$_2$. By performing both scattering and reflection spectroscopy we demonstrate strong coupling at room temperature with a Rabi splitting of $\sim 108$ meV. In addition, when the plasmonic resonance of these nanodisks is coupled with few-layer WS$_2$, a Rabi splitting of $\sim 175$ meV is observed, with a major increase of 62% relative to the monolayer configuration. Our results therefore suggest that ultrathin single-crystalline gold nanodisks coupled to WS$_2$ constitute an attractive platform to explore light–matter interactions in the strong–coupling regime.

Keywords

Plasmonics, TMDC, WS$_2$, strong coupling, excitons, gold nanodisks

Efficient coupling between light and matter is important for many applications as well as
for fundamental research within the field of nanophotonics. When the exchange rate of energy between an emitter and a cavity exceeds their intrinsic dephasing rates, the system enters the strong–coupling regime where new hybrid eigenstates form that are part light and part matter. \(^1\) Reaching the strong–coupling limit in different systems has, for instance, enabled studies of quantum electrodynamics, \(^2\) the experimental realization of low-threshold lasers, \(^3\) and coupling a single quantum of energy to nitrogen-vacancy centers in diamond. \(^4,5\) However, these investigations all required low temperatures to keep the emitter dephasing or the energy dissipation rate sufficiently low in order to achieve strong coupling.

The transition into the strong–coupling regime is dependent on the ability to control the coupling rate, \(g\), between the emitter and the cavity. Since \(g \propto \mu_{\text{ex}} \sqrt{N/V}\), where \(\mu_{\text{ex}}\) is the emitter’s dipole moment strength, \(N\) is the number of emitters coherently coupled to the cavity, and \(V\) is the cavity (effective) mode volume, several key factors can be engineered in order to facilitate this transition. For purely dielectric cavities, the typical mode volume is on the order of \((\lambda/n)^3\) due to the diffraction limit, thereby limiting the maximum attainable coupling strength and requiring long coherence times for both the cavity and the emitter states in order to enter the strong–coupling regime. On the other hand, plasmonics offers the possibility of subwavelength mode volumes, with associated strong enhancement of the field strength, albeit at the price of higher losses, mainly due to absorption in the metal. \(^7\) In the latter context, coupling plasmons to various organic and inorganic semiconductors has gained increasing attention in recent years, \(^8–14\) and plasmonic systems have been employed to reach the strong–coupling regime when interacting with organic molecules, \(^6,15–18\) resulting in enhanced nonlinearities and low threshold polariton lasing and condensation. \(^19,20\)

Moreover, excitons in two-dimensional (2D) materials, and, in particular, in TMDC monolayers and respective multilayers, have been the object of intense study in recent years, partly due to their unique optical properties, \(^21\) capable of merging together the main properties of Frenkel excitons in organic semiconductors (high binding energy and large oscillator strength) with that of Wannier–Mott excitons in inorganic quantum wells (relatively large exciton radius, low photodegradation and small saturation density) at room temperature. \(^21\) Examples of studies demonstrating strong coupling with excitons in 2D materials—both at cryogenic and room temperature—include, for instance, excitons in TMDCs coupled to plasmonic lattices, \(^22,23\) plasmonic and dielectric cavities, \(^12,24–29\) or to individual plasmonic nanoparticles. \(^30,31\) Some studies have even reported coupling to charged excitons (trions) in WS\(_2\), \(^32\) as well as self-hybridization of the excitons with cavity modes in many-layer TMDC systems. \(^33–35\)

The lattice structure of the TMDCs furthermore gives rise to a new degree of freedom in the form of valley polarization, which can be addressed using circularly polarized light when coupled to plasmonic structures. \(^36,37\)

In this work, we report the observation of the strong coupling between localized surface plasmons supported by high-quality, single-crystalline gold nanodisks, and excitons in monolayer and multilayer WS\(_2\). Both systems exhibit strong in-plane optical responses, and by controlling the nanoparticles’ size we achieve spectral and spatial overlap between the dipolar plasmon mode of the nanodisks and the A-exciton of WS\(_2\). \(^38,39\) Due to the high aspect ratio and quality of our single-crystalline gold nanodisks, we were able to experimentally observe strong plasmon-exciton coupling in both scattering and reflection measurements, characterized by a Rabi splitting of \(108 \pm 8\) meV at room temperature. Motivated by a recent work, \(^31\) we also show that when substituting the WS\(_2\) monolayer with a multilayer (seven layers in our case), an increase in the Rabi splitting to \(175 \pm 9\) meV is observed. To the best of our knowledge, this is the highest Rabi splitting reported for layered TMDCs coupled to an open plasmonic cavity. The accessibility of the open cavity along with the clear presence of the strong–coupling regime is an important stepping stone towards further study of the plethora of fundamental physics in these strongly coupled
light–matter systems, along with potential applications in quantum information processing, quantum metrology, nonlinear optical materials, and quantum light sources.

Results and discussion

1.8 2.0 2.2
Energy [eV]
Scattering [a.u.]
1.8 2.0 2.2
Energy [eV]
Photoluminescence [a.u.]
Scattering [a.u.]
WS
Disk
a)
c)
d)

Figure 1: a) Sketch of a single-crystalline gold nanodisk coupled to monolayer WS$_2$. b) Atomic force microscopy image of a monolayer WS$_2$ flake. The inset in the upper right corner shows the height profile along the white line, while the one in the lower left corner shows a scanning electron microscopy image of a typical nanodisk. Scale bar is 100 nm. c) Photoluminescence spectrum of monolayer WS$_2$ (black) and dark-field scattering spectrum of an individual, uncoupled nanodisk (blue). d) Experimental scattering spectrum of a single nanodisk coupled to WS$_2$ clearly showing the splitting between the upper and lower polariton branch.

We investigate strong plasmon-exciton coupling at room temperature by depositing ultrathin single-crystalline gold nanodisks on monolayers of WS$_2$, as depicted in Figure 1a. Such plasmonic nanodisks were chosen due to their strong in-plane dipole mode associated with the dipolar localized surface plasmon resonance (LSPR); these are tunable by controlling the nanodisk’s radius (on the order of 30 nm)$^{38}$ and exhibit narrow linewidths due to the single-crystalline nature of the nanodisks. Moreover, like the other 2D TMDCs, WS$_2$ has a strong in-plane excitonic response, characterized by a large transition-dipole moment.$^{10,40,41}$ This, together with the stability of excitons in atomically-thin WS$_2$ (owing to their large binding energies$^{42}$), makes our system extremely well-suited for exploring light–matter interactions in the strong-coupling regime at room temperature.

Flakes of WS$_2$ were mechanically exfoliated from commercially available bulk crystals (HQ Graphene) onto plasma cleaned SiO$_2$/Si substrates. Monolayer flakes were automatically detected and identified by quantitative optical mapping.$^{43}$ The monolayer nature of these flakes was further confirmed by atomic force microscopy (AFM)—cf. Figure 1b—, where the height of the flake was found to be $\approx 0.87$ nm, in agreement with previously reported results.$^{39}$ The photoluminescence (PL) spectrum, represented by the black line in Figure 1c, reveals the exciton emission, where the asymmetry of the peak to the low-energy side is caused mainly by the interaction with phonons.$^{44}$ From this spectrum we find an emission energy of $E_{\text{em,ex}} = 1.951$ eV in accordance with the literature$^{39}$ (for more information, see Figure S1).

To extract the energy and corresponding linewidth associated with the optical transition of the A-exciton, we performed reflection measurements on five different monolayer flakes, using spatially filtered white light to ensure normal incidence. Employing the transfer-matrix method$^{45,46}$ we retrieved the WS$_2$ dielectric function for each flake, from which we extract an average exciton energy $E_{\text{ex}} = 1.963$ eV and linewidth $\Gamma_{\text{ex}} = 28$ meV; see Figure S2 and Table S1 in the Supporting Information.

The open plasmonic cavities used in this work consists of cylindrical single-crystalline gold nanodisks, chemically synthesized as described in Ref. 38. Briefly, triangular gold nanoplates were first synthesized using a three-step seed-mediated method.$^{47}$ The nanodisks were produced by performing anisotropic oxidation on the nanoplates. The oxidation allows for finely tailoring the nanodisk diameter, and
the thickness of the gold nanodisks remained unchanged during the oxidation process. A thin layer (∼1 nm) of cetyltrimethylammonium bromide (CTAB) is present on the surface of the nanodisks after the synthesis. In our study, cylindrical gold nanodisks of 8.8 ± 0.2 nm in thickness, measured without the CTAB layer, were chosen because of their moderate plasmon damping and concomitant narrow plasmon linewidth. Due to the inherent variation in particle radii, each batch contains particles with their LSPRs distributed around a mean energy, the latter chosen to match the exciton energy (E_{ex} = 1.963 eV). A representative scattering spectrum of a single gold nanodisk is shown in Figure 1c. Measuring the uncoupled nanodisks on the bare SiO_2/Si substrate results in an average linewidth of the plasmon resonance of Γ_{pl} = 170 meV. The variation of the particles’ LSPRs is exemplified in ensemble measurements performed on the nanodisk solution in Figure S3, where the extinction spectra show a width about twice that of the individual nanodisks due to inhomogeneous broadening. For a resonant energy around 1.96 eV we obtain a Q-factor of E_{pl}/Γ_{pl} ≈ 11.5, close to its intrinsic quasi-static limit of ∼13.5 for an arbitrarily shaped gold nanoparticle when only the dielectric function is considered. This shows that other dissipation pathways, such as surface scattering and disorder, are minimized due to the single-crystalline nature of the nanodisks.

Reaching the strong coupling regime requires a simultaneous spatial and spectral overlap of the LSPR and the exciton in the nanodisk and WS_2, respectively. The spatial overlap was ensured by dropcasting the nanodisks directly onto the WS_2 flakes. The CTAB molecule layer ensures a narrow gap without direct contact between the metal and the underlying flake in order to prevent possible quenching. As mentioned above, the spectral overlap was ensured by selecting the appropriate nanodisk’s radius. Moreover, in 2D TMDCs the dipole moment of the exciton is strongly oriented in the plane of the 2D layer, which requires special attention when coupling to external fields. However, the dipolar LSPR mode of the nanodisk is oriented in the same plane as the excitons, thus promoting a strong interaction. Finite element and analytic calculations corroborate the observed resonance energy of the nanodisks even in the presence of a high-refractive index material, such as WS_2, underneath (see Figure S4). The inherent size distribution (with different radii) in a batch of gold nanodisks straightforwardly enables measurements on different nanodisks with LSPRs distributed around the energy of the exciton (thereby allowing us to study the light-matter interaction at positive and negative detunings). Using dark-field (DF) microscopy we then obtained scattering spectra for each individual particle. In addition to the DF measurements, scanning electron microscope images were taken to ensure that the acquired spectra originated only from single nanodisks rather than from dimers or particles with other morphologies. Due to the small size and correspondingly small scattering efficiency of the nanodisks, careful background removal was key to isolating the signal of the coupled system. This background was caused by scattered light from nearby WS_2 edges as well as exciton photoluminescence (see Supporting Information for further details). A typical spectrum taken from a gold nanodisk resting on a WS_2 monolayer is shown in Figure 1d, where two distinct peaks appear around the bare exciton energy. The almost equal strength of the two peaks indicates that the LSPR of the nanodisk is close to the exciton resonance. By measuring particles with different radii, and thus different LSPR energies, we are in this manner able to map out the dispersion of the coupled system as a function of the plasmon-exciton energy detuning. All the acquired spectra show a double peaked lineshape. Extracting the energy of the peaks from the scattering spectra, a clear anti-crossing behaviour is observed, as shown in Figure 2a, which is a hallmark of these emitter-cavity coupled systems.

In order to analyze the data, we apply the coupled-oscillator model (COM) in its non-Hermitian Hamiltonian form given by the eigenvalue problem:

\[
\begin{bmatrix}
E_{pl} - i \frac{\Gamma_{pl}}{2} & g \\
-g & E_{ex} - i \frac{\Gamma_{ex}}{2}
\end{bmatrix}
\begin{bmatrix}
\alpha \\
\beta
\end{bmatrix}_\pm = E_\pm
\begin{bmatrix}
\alpha \\
\beta
\end{bmatrix}_\pm,
\]  

where $E_{pl}$ and $E_{ex}$ are the plasmon and exciton energies, $\Gamma_{pl}$ and $\Gamma_{ex}$ are their damping widths, and $g$ is the exciton-plasmon coupling strength.
where $E_{\text{pl}(\text{ex})}$ and $\Gamma_{\text{pl}(\text{ex})}$ are the plasmon (exciton) energy and linewidth, respectively, $g$ is the coupling strength, and $\alpha$ and $\beta$ are the amplitudes describing the polaritonic state in terms of its plasmonic ($\alpha_{\pm}$) and excitonic ($\beta_{\pm}$) constituents. Diagonalizing the Hamiltonian yields the two energy eigenvalues

$$E_{\pm} = \frac{1}{2} (E_{\text{pl}} + E_{\text{ex}}) - \frac{i}{2} (\Gamma_{\text{pl}} + \Gamma_{\text{ex}})$$

$$\pm \frac{1}{2} \sqrt{4g^2 + \left[ \delta - \frac{i}{2} (\Gamma_{\text{pl}} - \Gamma_{\text{ex}}) \right]^2}, \quad (2)$$

where we have introduced the plasmon-exciton detuning, $\delta = E_{\text{pl}} - E_{\text{ex}}$. The eigenvalues describe an energy spectrum divided into an upper polariton branch (UPB, $E_+$) and a lower polariton branch (LPB, $E_-$). The Rabi splitting $E_{\text{Rabi}}$ is then defined as the energy difference between the UPB and LPB at zero detuning, $^8$ giving

$$E_{\text{Rabi}} = \sqrt{4g^2 - \frac{(\Gamma_{\text{pl}} - \Gamma_{\text{ex}})^2}{4}}. \quad (3)$$

From the scattering spectra of the individual nanodisks on WS$_2$ we extracted the respective energies of the upper and lower polariton branches, $E_+$ and $E_-$. From energy conservation we then obtained the plasmon energy as $E_{\text{pl}} = E_+ + E_- - E_{\text{ex}}$. The avoided crossing is clearly visible from the histogram in the right side of Figure 2a, with no data points located between the two polaritonic branches. The vertical error bars represent the uncertainty associated with the extracted peak positions, which we estimate to be on the order of $\pm 5\,\text{meV}$. The horizontal error bars represent the propagated uncertainties in the calculated detunings, which are dominated by the standard deviation of the measured exciton energy.

To estimate the coupling strength $g$ and the Rabi splitting $E_{\text{Rabi}}$, we simultaneously fit the real part of the eigenvalue spectrum (Equation 2) to the experimentally determined dispersion of the UPB and LPB. In the fitting procedure we fix the values of the exciton energy ($E_{\text{ex}} = 1.963\,\text{eV}$), the exciton linewidth ($\Gamma_{\text{ex}} = 28\,\text{meV}$), and the plasmon linewidth ($\Gamma_{\text{pl}} = 170\,\text{meV}$) to the experimentally determined values, which leaves the coupling strength as the only free parameter. The $g$-value found in this manner represents an ensemble average of the system in general, as variations in particle size and the local environment can influence the number of participating excitons and through that the individual coupling strengths (see the Supporting Information for further discussion). The described procedure yields a value of $g = 64 \pm 3\,\text{meV}$, from which we calculate a Rabi splitting of $E_{\text{Rabi}} = 108 \pm 8\,\text{meV}$ using Equation 3. Comparing this with the overall losses in the system $\frac{1}{2} (\Gamma_{\text{pl}} + \Gamma_{\text{ex}}) = 99 \pm 3\,\text{meV}$, we see that our hybrid nanodisk/WS$_2$ system is just at the onset of the strong-coupling regime, as per the criterion $E_{\text{Rabi}} > \frac{1}{2} (\Gamma_{\text{pl}} + \Gamma_{\text{ex}})$.

Five selected scattering spectra showing the evolution of the optical response of the hybrid system are depicted in Figure 2b. The figure clearly shows an avoided crossing in the succession of the individual spectra, together with a shift of spectral weight from the LPB to the UPB as the detuning approaches $\delta = 0\,\text{meV}$ from below. In addition, we note that the noise generally increases for larger positive $\delta$ since the LSPR energy increases with decreasing particle radius, resulting in a lower scattering cross section.

Since $\delta = E_+ + E_- - 2E_{\text{ex}}$, the exact value for $\delta$ reported in Figure 2b–c is highly sensitive to the value of $E_{\text{ex}}$. From the reflection measurements on the bare WS$_2$ flakes alone, we observe exciton energies in the range 1.958 eV to 1.968 eV, corresponding to a detuning variation of $\Delta\delta = 20\,\text{meV}$, which may influence the COM fit. Therefore, we also use the COM to extract the peak positions associated with the UPB and LPB, and also to obtain the exciton energy $^5$—see Figure S8. From this approach, we find a slightly higher average, exciton energy of $E_{\text{ex}} = 1.981\,\text{eV}$, but also a larger spread of 40 meV (i.e., $\Delta\delta = 80\,\text{meV}$). This larger variation and change in $E_{\text{ex}}$ (with respect to the same quantity measured prior to the nanodisks’ deposition) can be caused by, for instance, local strain or induced doping from the nanoparticle solution. $^5$ Nevertheless, using instead this averaged $E_{\text{ex}}$ in the same analysis as before results in a change of only 4 meV in the obtained Rabi
Figure 2: a) Dispersion retrieved from scattering measurements of the coupled plasmon-exciton system—consisting of single-crystalline gold nanodisks on monolayer WS$_2$—with the lower (blue) and upper (red) polariton branch. The right panel shows the distribution of the measured peaks. The solid black line corresponds to a fit to the data using Equation 2, while the horizontal and sloped dashed lines indicate the exciton and plasmon energies, respectively. The black crosses are the peak positions extracted from the theoretically calculated spectra plotted in Figure 3b. b) Experimental dark-field scattering spectra from five different individual gold nanodisks demonstrating the evolution of the optical response with different plasmon energies. The individual detunings $\delta = E_{\text{pl}} - E_{\text{ex}}$ are presented next to the corresponding spectra. c) Measured reflection spectra for the same five particles as in b). The absorption of the disks dominates the extinction spectrum by more than an order of magnitude making the reflection spectrum representative of the absorption (see Figure 3a). The insets are scanning electron microscope images of the five gold nanodisks; the scale bar is 100 nm.

splitting, despite the shift of 36 meV in the detuning for all measurement points, see Figure S9.

The strong–coupling regime is associated with a pronounced mode splitting not only in the scattering but also in the absorption spectrum of the coupled system. Often, the presence of the splitting in absorption is only verified numerically, since measuring the absorption independently from the scattering normally requires specialized techniques.

We address this by performing bright-field reflection measurements on the same samples. Due to their morphology, the raw reflection spectrum, $R_{\text{raw}}$, contains both scattering and absorption contributions from the coupled system, as well as the strong absorption lines of the excitons in the uncoupled WS$_2$, $R_{\text{WS}_2}$. However, our nanodisks have small radii (<35 nm) and a thickness of only 8.8 nm, and numerical calculations suggest that the absorption cross section is larger than the scattering cross section by more than an order of magnitude (cf. Figure 3a). As such, the raw reflection spectrum will contain information about the absorption properties of the coupled nanodisk/WS$_2$ system.

In order to isolate this information, careful background removal is required. We therefore calculate the coupled nanodisk/WS$_2$ reflection spectrum as

$$\Delta R = \frac{R_{\text{WS}_2} - R_{\text{raw}}}{R_{\text{sub}}},$$  \(4\)

where $R_{\text{sub}}$ is the reflection from the bare SiO$_2$/Si substrate. This normalization takes into account the substrate contribution (for further details, see the Supporting Information). The reflection spectra calculated in this manner from the same five particles as in Figure 2b are
shown in Figure 2c. As $E_{\text{pl}}$ is tuned across the exciton energy, we observe a similar behavior in reflection as for the scattering spectra. We note that the absorption is blueshifted in all cases when compared to the scattering, which is also observed in our calculations; cf. Figure 3b-c. The observation of mode splitting and hybridization not only in scattering, but also in the reflection spectra further supports and corroborates our observation of the strong coupling in our nanodisk/WS$_2$-system.

![Graphs showing scattered and absorbed light](image)

**Figure 3:** a) Calculated scattering (red) and absorption (blue) cross sections $\sigma$ obtained with finite-element method calculations of a nanodisk of radius $R = 23$ nm normalized to the geometrical area. The scattering cross section has been multiplied by 50 to match the scale. The ratios between the maxima of $\sigma_{\text{abs}}$ and $\sigma_{\text{scat}}$ vary from 96 ($R = 19$ nm) down to 21 ($R = 29$ nm). b-c) Normalized scattering and absorption of particles of radii $R = 19$ nm, 23 nm, 25 nm, 27 nm, and 29 nm, arranged from top to bottom.

In addition to the experiments, we perform finite-element method (FEM) calculations of the electrodynamics governing the system’s response (see Methods). In the computations, we take the experimentally determined radii (from 19 nm to 29 nm) and nanodisk thickness (9 nm), as well as a 1 nm thick polymer layer surrounding the particle. We furthermore use our experimentally determined dielectric function of the WS$_2$ flakes; see Supporting Information. For optical constants of gold, we use the values of McPeak et al. in optimized film quality conditions. This choice of reference data was made to better reflect the single-crystalline nature of our nanodisks. In this way, we obtain scattering and absorption spectra of the particles as shown in Figure 3b and c. Since the nanodisks are thinner than the skin depth of gold of around 25 nm at 1.96 eV, the electric field completely permeates the particles, making the results very sensitive to the particular value of the dielectric function. For instance, using instead the values from Johnson and Christy redshifts the resonance position by around 40 meV (see Figure S12), and changes in especially the imaginary part of ε have been reported for thin gold films. However, we still see that we are able to reproduce the experimentally observed behaviour both in scattering and absorption with good agreement. The calculations show scattering cross sections approaching zero at the exciton’s energy, indicative of strong plasmon-exciton coupling. These same near-zero intensities are not observed in the experiments, which may be caused by a background signal coming from the strong scattering from the WS$_2$ flake edges. Although we perform background removal on all measured spectra, the scattering cross section of the nanodisks is small and any remaining background is expected to influence the overall signal intensity. Note, however, that in the calculated absorption spectra these same near-zero intensities are not observed due to power dissipated within the WS$_2$.

Extracting the peak locations of the calculations in the same fashion as for the experimental results allows us to compare the positions of the UPB and LPB to the experimental data, as indicated by the black crosses in Figure 2a, thereby showing an excellent agreement between the experiment and the numerical calculations.

Besides studying strong coupling between the LSPRs supported by the nanodisks and the excitons in monolayer WS$_2$, we have also performed measurements with few-layer WS$_2$. Recent experiments have reported the possibility of increasing the mode splitting by increasing the number of TMDC layers coupled to the plasmonic resonator. In order to assess the ma-
Figure 4: Experimentally obtained dispersion for the coupled plasmon-exciton system on multilayer WS$_2$. Note the change in scale of the $y$-axis compared to Figure 2a.

magnitude of this effect in our system, we have measured the optical response of the gold nanodisks on a WS$_2$ flake 4.4 nm in height, which corresponds to seven layers. Using the transfer-matrix method as before, we extract the dielectric function of the multilayer WS$_2$ flake, which is dominated by a main excitonic resonance at $E_{\text{ex,multi}} = 1.942$ eV, with a linewidth of $\Gamma_{\text{ex,multi}} = 44$ meV (see Table S2). We note that both the broadening and redshift of the $A$-exciton resonance is well-known for multilayers.\textsuperscript{31} Following the same procedure for data analysis as in the monolayer case, we have obtained the results plotted in Figure 4, exhibiting a pronounced avoided crossing akin to strong-coupling phenomena. In the multilayer configuration, we observe a 45\% increase of the coupling strength, resulting in $g_{\text{multi}} = 93 \pm 4$ meV, which in turn is associated with a Rabi splitting of $E_{\text{Rabi, multi}} = 175 \pm 9$ meV, corresponding to a remarkable 62\% increase. To the best of our knowledge, this is the highest Rabi splitting reported in a TMDC coupled to an open plasmonic cavity.\textsuperscript{28,30,31,60} Furthermore, the direct availability of the open plasmonic cavity is advantageous for future near-field explorations and sensing applications, as well as external coupling to other cavities and optical circuit elements, when compared to closed-cavity configurations\textsuperscript{33,35,61}.

In order to understand the increase in the coupling strength that we observe for the seven-layer WS$_2$ flake, we have performed numerical calculations using the dielectric function extracted from our reflection measurements. The ensuing positions of the UPB and LPB are indicated by the black crosses in Figure 4. The calculations predict an overall increase of the coupling strength with the number of layers. However, quantitatively we observe a slightly lower increase in the Rabi splitting in comparison to our experimental data. This difference could be due to the fact that we have approximated the optical response of multilayer WS$_2$ as an isotropic dielectric function and we therefore do not take into account the out-of-plane response of multilayer WS$_2$. Despite these quantitative differences we observe qualitative agreement between our calculations and our experimental data. We explain this significant increase in the Rabi splitting with an increased number of excitons participating in the coupling. Furthermore, our numerical calculations suggest that additional layers will not increase the coupling strength substantially, since we observe an exponential decay of the plasmon mode energy to 1/e inside the WS$_2$ over a length of $\sim$4 layers (see Figure S13). These conclusions are in agreement with recent experimental works\textsuperscript{27,31}, although we emphasize that the saturation effect appears to be system dependent.\textsuperscript{59}

**Conclusion**

We have experimentally demonstrated strong coupling between single-crystalline, high-aspect ratio gold nanodisks on mono- and multilayers of WS$_2$ at room temperature. In the monolayer case we extract a Rabi splitting of $108 \pm 8$ meV ($g = 64 \pm 3$ meV). Additionally, we have observed the strong coupling both in scattering and reflection measurements, where the latter is indicative of the coupled system absorption. In the multilayer configuration, we achieved a significant 62\% increase of the Rabi splitting to $175 \pm 9$ meV ($g_{\text{multi}} = 93 \pm 4$ meV), i.e. in
excess of six times $k_B T$ at room temperature. The increase is enabled by a larger mode overlap of the plasmon field and the WS$_2$. This way of controlling the coupling regime in plasmonic nanodisks and structurally similar systems is a key component towards applications within all-optical circuitry, polaritonic lasers, and quantum information processing, as well as the exploration of possible anti-bunching effects in multiple emitters coupled to plasmonic cavities.$^{13,62}$

**Methods**

**Optical measurements.** A custom spectroscopy setup built from a Nikon Eclipse Ti-U inverted microscope was used for the optical measurements. For the dark-field and bright-field spectra a halogen lamp with a tunable power up to 100 W was used, while for the photoluminescence a 407 nm diode laser (Integrated Optics) was used. The light was focused on the sample with a TU Plan Fluor objective from Nikon (100×, 0.9 NA) and collected with the same objective. Afterwards, the light was directed towards a slit allowing for a precise selection of the collection area. The light then entered a Shamrock 303i Spectrometer equipped with a 450 nm longpass filter (FELH0450 from Thorlabs) and an electronically cooled Newton 970 EMCCD for acquiring spectra. All spectra consist of the sum of several lines on the 2D CCD uniquely identified for each particle. Each of these spectra were first corrected for dark counts, and then for background using the local environment in close vicinity of the individual particles obtained directly from the same spectroscopic image. Finally, the spectra were divided by the normalized white light spectrum of the halogen lamp. The photoluminescence spectra were obtained in a similar manner apart from the white light spectrum correction. All experiments were performed at room temperature.

**Finite-element calculations.** A commercially available FEM software (COMSOL Multiphysics v. 5.3a) was used to compute the electrodynamic response of the gold nanodisks placed on top of the mono- and multilayer WS$_2$. We have performed calculations of nanodisks with radii ranging from 19 nm to 29 nm on monolayer WS$_2$. Due to higher values of the dielectric function and a higher thickness of the multilayers WS$_2$, the LSPR of the nanodisks were redshifted and the radii close to the excitonic resonance ranged from 11 nm to 21 nm. In all our calculations, we have used a thickness of 9 nm for the metallic core.$^{38}$ For the optical response of gold we have used the dielectric function data reported by McPeak et al.$^{55}$, to better reflect the single-crystalline nature of our nanodisks. We model the layer of CTAB molecule as a homogeneous 1 nm thick dielectric layer surrounding the nanodisks with a refractive index of 1.435.$^{63}$ The nanodisk with the CTAB layer was taken as being in direct contact with the WS$_2$. Both the single- and seven-layer WS$_2$ were modeled as homogeneous, isotropic bulk materials with effective thicknesses of 0.6 nm and 4.3 nm, respectively. The dielectric functions for both cases were extracted from experimental reflection measurements followed by a treatment with the transfer-matrix method (see Table S1 and S2). The SiO$_2$ substrate is modelled as a semi-infinite layer and the dielectric function is taken from Malitson.$^{64}$ Moreover, for simplicity we have assumed that the exciting field is impinging at normal incidence onto the nanodisk. The scattering cross sections were evaluated by integrating the scattered energy density flowing through a surface with a radius of 100 nm, and placed 150 nm above the nanodisk, to simulate the numerical aperture of the objective used in our measurements (see optical measurements section above). The absorption cross sections were calculated by integrating the energy density dissipated within the volume of the metallic core of the nanodisk and within the layered material WS$_2$ located below the nanodisk. The mesh size inside the WS$_2$ layers, the CTAB layer and in the metal core close to the metal/CTAB interface were taken as small as 0.3 nm to allow numerical convergence. The remaining part of the nanodisks were meshed with elements with sizes ranging from 0.3 nm to 4 nm.
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(54) This shift is predicted from Mie theory and has also been demonstrated experimentally.53


Supporting information for:

Single-crystalline gold nanodisks on WS$_2$
mono- and multilayers for strong coupling at
room temperature

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Figure S1: Photoluminescence spectrum from monolayer WS$_2$ flake. The asymmetry of the peak is caused by the strong interaction with phonons, but can also indicate the presence of the trion (charged exciton) in addition to the neutral state of the A-exciton. An ideal two-level system would result in Lorentzian lineshapes, but the interaction with the surroundings in the form of e.g. local strain and doping causes non-ideal conditions. For this reason we chose to fit a double Voigt profile, since this can take the non-ideality of the system into account.
S1  Determining the permittivity of WS$_2$ using the transfer-matrix method

In order to extract the optical properties of a two-dimensional (2D) material we employ the transfer-matrix method.$^{S3,S4}$ Here, the 2D material is modeled using a surface conductivity $\sigma_{2D}$. The surface conductivity is connected to the dielectric function via

$$\frac{\sigma_{2D}}{\omega \varepsilon_0} = i (1 - \varepsilon_{TMDC}) d_{TMDC},$$  \hspace{1cm} (S1)

where $\omega$ is the angular frequency, $\varepsilon_0$ is the vacuum permittivity, $d_{TMDC}$ is the effective thickness of the 2D material, and $\varepsilon_{TMDC}$ is the TMDCs (effective) dielectric function. The value for the effective thickness was taken to be the interlayer distance in bulk WS$_2$, that is, $d_{TMDC} = 0.618$ nm.$^{S5}$ The permittivity is parameterized as a sum of Lorentzians characterised by oscillator strengths $f_i$, resonant energies $E_i$, and corresponding linewidths $\Gamma_i$, together with a constant background $\varepsilon_\infty$, i.e.,

$$\varepsilon_{TMDC}(E) = \varepsilon_\infty + \sum_{i=1}^{N} \frac{f_i}{E_i^2 - E^2 - i\Gamma_i E},$$  \hspace{1cm} (S2)

such that each Lorentzian oscillator corresponds to an exciton. However, from previous works we know the approximate location of the different oscillators,$^{S6}$ and since our set up is bounded to the high energy side at $\sim$2.6 eV, we group the high-energy oscillators into a single one such that we use three: One each for the $A$- and $B$-exciton, and one for the high-energy response ($i = 1, 2,$ and 3, respectively). Since we use an unpolarised white light source, we assume a 50/50 mix of $s$- and $p$-polarisations. We fit the experimental spectra according to the following expression:

$$\mathcal{R} = \frac{\mathcal{R}_WS^s + \mathcal{R}_WS^p}{\mathcal{R}_{sub}^s + \mathcal{R}_{sub}^p} + b,$$  \hspace{1cm} (S3)

S3
where the subscript denotes either reflection from WS$_2$ or SiO$_2$/Si substrate, while the superscript denotes the polarization. An extra constant term $b$ has been introduced to take into account a possible experimental offset in order to achieve a better match.

Figure S2: Experimental reflection spectrum of a WS$_2$ monolayer flake normalized to the bare SiO$_2$/Si substrate along with the fit obtained from the transfer-matrix method.

A representative experimental spectra along with the best fit is shown in Figure S2, demonstrating a good fit to the experimental data in the presented spectral range. We have repeated this procedure for all the five flakes and the resulting fitting parameters are indicated in Table S1, for the monolayer WS$_2$. In general, the values are in good agreement with each other with relatively low spread. The value of the background lies consistently at around $-0.13$. It should be noted, however, that this parameter is highly sensitive to the exact value of the refractive index of the substrate materials, especially the SiO$_2$ as it is here the multiple internal reflections can arise. Variations in $b$ exceeding 0.05 were observed simply by using a different set of refractive index data for the SiO$_2$. As such no further significance is ascribed to this discrepancy, since the values obtained for the WS$_2$ dielectric function are in good agreement with those previously reported.$^{36}$

The same analysis is performed for the multilayer WS$_2$ with the only change being a
Table S1: Experimentally obtained values for the parameterized permittivity of monolayer WS$_2$. $E_3$ was fixed at 2.75 eV for the analysis, while $\varepsilon_\infty$ was bounded to the low side at a value of 1. The units are $f_i$: eV$^2$, $E_i$: eV, and $\Gamma_i$: meV.

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<td>2.33</td>
<td>106</td>
<td>43.8</td>
<td>122</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>2.65</td>
<td>1.963</td>
<td>27.8</td>
<td>2.95</td>
<td>2.33</td>
<td>106</td>
<td>45.2</td>
<td>2.75</td>
<td>106</td>
<td></td>
</tr>
</tbody>
</table>

Table S2: Experimentally obtained values for the parameterized permittivity of multilayer (7) WS$_2$. $E_3$ was fixed at 2.75 eV for the analysis, while $\varepsilon_\infty$ was bounded to the low side at a value of 1. The units are $f_i$: eV$^2$, $E_i$: eV, and $\Gamma_i$: meV.

<table>
<thead>
<tr>
<th>Flake</th>
<th>$\varepsilon_\infty$</th>
<th>$f_1$</th>
<th>$E_1$</th>
<th>$\Gamma_1$</th>
<th>$f_2$</th>
<th>$E_2$</th>
<th>$\Gamma_2$</th>
<th>$f_3$</th>
<th>$E_3$</th>
<th>$\Gamma_3$</th>
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</thead>
<tbody>
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<td>1.60</td>
<td>1.942</td>
<td>44.3</td>
<td>1.49</td>
<td>2.34</td>
<td>111</td>
<td>61.1</td>
<td>2.75</td>
<td>105</td>
</tr>
</tbody>
</table>

different thickness of the quasi-2D layer; in particular, we have $d_{TMDC} = 4.33$ nm, which corresponds approximately to 7 layers. Only one flake was used here, and the fitting parameters are shown in Table S2.

S2 Optical measurements and data processing

In the confocal microscopy set up used in this work, it is not possible to isolate the signal from the single nanodisks during the measurement process. This is because the nanodisks are $\sim 50$ nm in diameter while the slit used has a projected width of $\sim 1$ µm. In order to isolate the spectrum for the coupled system, all spectra are corrected according to the following expression

$$I_{\text{disk}} = \frac{I_{\text{raw}} - I_{\text{bg}} - I_{\text{dark}}}{I_{\text{ref}}}$$

where $I_{\text{disk}}$ is the isolated spectrum of a nanodisk, $I_{\text{raw}}$ is the raw measurement data, $I_{\text{bg}}$ is the background (surrounding material, stray light, scattering from nearby objects etc.),
Figure S3: Ensemble measurements of the normalized extinction cross section performed on the gold nanodisks in the solution after synthesis showing the tunability of the plasmonic resonance. The peak maxima are located at, from left to right, 622 nm, 646 nm, 670 nm, 692 nm, 718 nm, and 740 nm. Longer wavelengths correspond to larger radii. The particle solution with a peak at 670 nm was used for this work.

Figure S4: Absorption (blue) and scattering (red) cross section of a gold nanodisk of radius $R = 24$ nm calculated using the finite element method. The disk is sitting on a monolayer of WS$_2$ where the A-exciton has been removed to take the high refractive index into account without coupling. The scattering cross section has been multiplied by 30 to match the scale.
$I_{\text{dark}}$ is the dark counts in the detector (which are automatically corrected for during data acquisition), and $I_{\text{ref}}$ is the reference spectrum of the halogen lamp.

Since the used Newton 970 EMCCD is a 2D CCD, it is possible to locally extract the background for each measurement individually. In doing so we ensure the subtracted background resembles the one of the coupled system as closely as possible.

### S2.1 Dark-field scattering

For dark-field spectra ideally the background should be zero. However, stray light from the surroundings, and proximity scattering from nearby objects, where the latter is the largest contributor mainly from the strong scattering at the WS$_2$ edges. All of these sources of noise can be accounted for readily using Equation S4. Additionally, for some WS$_2$ flakes the white light excitation was strong enough to cause photoluminescence. Due to inhomogeneities in the flake emission this lead to nanodisk spectra being discarded as it was not possible to remove the background in a consistent way. For uniform emission in close vicinity of the nanodisk, however, this extra signal can be removed using Equation S4.

### S2.2 Bright-field reflection

A sketch of the sample morphology is shown in Figure S5. For all in the following the transmission through the sample is zero, since the bottom silicon wafer absorbs in the wavelength region of interest.

Away from the particle, the incident light impinges on the sample and is reflected from the bare WS$_2$/SiO$_2$ interface as well as the underlying SiO$_2$/Si ditto. Due to the multiple reflections in the SiO$_2$, the reflection spectrum contains strong absorption lines from the excitons in the WS$_2$ (cf Figure S2).

The presence of the particle complicates the picture somewhat. A part of the light is backscattered from the particle and will be present in the reflection spectrum, while some of it interacts with particle and is absorbed before undergoing the reflection at the SiO$_2$/Si
interface. The direct and additional multiple reflections will interact with the particle and undergo further scattering and absorption. In this manner, the raw reflection spectrum obtained of the coupled nanodisk/WS₂ system will contain both scattering and absorption contributions from the sample. As mentioned in the main text, the nanodisks with $R < 29 \text{ nm}$ have an absorption cross section at least 20 times higher than the scattering cross section. Based on this we conclude that in the raw reflection spectrum the scattering contribution is negligible compared to the absorption.

The data processing is the same, but the raw spectrum will always be a convolution of the bare WS₂ and the coupled system of nanodisk and WS₂ because of the diffraction limit. The WS₂ already has a strong absorption due to the $A$-exciton line, and this signal will always be overlaid on the actual nanodisk spectrum. A plot of $I_{\text{raw}} (R_{\text{raw}})$, $I_{\text{bg}} (R_{\text{WS}_2})$, and $I_{\text{disk}} (\Delta R)$ can be seen in Figure S6 for the nanodisks with detuning $\delta = -45 \text{ meV}$ (top), 22 meV (middle), and 86 meV (bottom), respectively. The splitting is not visible in the raw reflection spectra since the coupled nanodisk/WS₂-system has decreased absorption at the exciton energy (as is shown by calculations in Figure 3), and unless the splitting is sufficiently large to clearly separate the three peaks, this will always be the case. We clearly observe
the influence of the nanodisk on the spectrum, though, where the spectral weight is shifted as the plasmon resonance is detuned across the exciton energy. Further evidence for this is shown in Figure S7, where the signal of a single nanodisk with a radius of $\sim 30$ nm leads to a reduction of about 10% compared to the bare substrate. This reduction is comparable to the intensity variation due to the presence of the WS$_2$, see Figure S6, which is the justification for defining $\Delta R$ in the way it has been in Equation (4) in the main text. The minus in the numerator has been introduced for convenience.

S3 Data analysis with the coupled-oscillator model

The coupled-oscillator model (COM) predicts the scattering and extinction spectra for two coupled, damped harmonic oscillators, and has successfully been used to model the interaction between an emitter and a nanoscale cavity.\textsuperscript{S7} The scattering cross section is given by

$$C_{\text{scat}}(E) \propto E^4 \left| \frac{(E_{\text{ex}}^2 - E^2 - i\Gamma_{\text{ex}}E)}{(E^2 - E_{\text{pl}}^2 + i\Gamma_{\text{pl}}E)(E^2 - E_{\text{ex}}^2 - i\Gamma_{\text{ex}}E) - E^2g^2} \right|^2$$

(S5)

where $E_{\text{ex(pl)}}$ and $\Gamma_{\text{ex(pl)}}$ is the exciton (plasmon) energy and linewidth, respectively, and $g$ is the coupling strength. The result of fitting to an experimental spectrum can be seen in Figure S8. The extracted energies of the upper and lower polariton branches along with the fitted exciton energy are also indicated. It should be noted that by fitting 7 parameters (the five in Equation S5 along with a background and proportionality constant) in an expression as involved as Equation S5 produces larger uncertainties in the fitted parameters. Since the nanodisks have small scattering cross sections, the data is typically noisy which furthermore complicates the fitting process.

We extract the energies of the two polariton branches from the fit instead of directly from the spectra while fixing the exciton energy to the average fitted value ($E_{\text{ex}} = 1.981$ eV). The exciton and plasmon linewidth was kept at the same values as in the main text ($\Gamma_{\text{ex}} = 28$ meV, $\Gamma_{\text{pl}} = 170$ meV). The result from this can be seen in Figure S9 which gives a coupling strength
Figure S6: The raw data containing both nanodisk and WS$_2$ contributions (blue), the background containing only the WS$_2$ signal (red), and the resulting spectrum after using Equation S4 (green) for the nanodisks detuned at $\delta = -45$ meV (top), 22 meV (middle), and 86 meV (bottom) in Figure 2c. The spectra have been normalized and shifted for comparison.
Figure S7: Raw reflection spectrum of the nanodisk in the inset and the SiO₂/Si substrate showing a signal reduction from the nanodisk of ∼10 %. The scale bar is 100 nm.

Figure S8: Experimental spectrum with a fit to the coupled oscillator model in Equation S5. The vertical lines indicate the extracted energies of the two polariton branches (solid) and the exciton (dashed).
of \( g = 63 \pm 3 \text{ meV} \) resulting in a Rabi splitting of \( E_{\text{Rabi}} = 104 \pm 7 \text{ meV} \).

Figure S9: Experimentally obtained dispersion for the coupled plasmon-exciton system using the coupled oscillator model to extract the peak positions. The larger horizontal error bars compared to Figure 2a in the main text come from the increased spread in \( E_{\text{ex}} \).

The \( g \)-values reported here and in the main text represent an ensemble average of the values from the individual nanodisks. Local variations in e.g. strain, doping, the presence of defects and the exact morphology of the disks can lead to changes in \( g \). Additionally, the changing size of the the disks required to map the avoided crossing also changes the electromagnetic environment. The individual \( g \)-values extracted from the COM are plotted in Figure S10 as a function of the detuning. As is evident there is a significant spread between the individual particles, and no clear trend can be identified. A histogram of the values is shown in Figure S11, where we see a peak just above \( g = 60 \text{ meV} \). Assuming a true mean value exists for the system and fitting a normal distribution yields a mean value \( \mu = 61 \pm 8 \text{ meV} \) and standard deviation \( \sigma = 21 \pm 4 \text{ meV} \), which is close to the values with the other methods described in the main text.
Figure S10: Distribution of fitted values for the coupling strength $g$ from the coupled-oscillator model.

Figure S11: Histogram of the fitted values of the coupling strength $g$ shown in Figure S10.
Figure S12: Comparison of the calculated spectra when using McPeak et al.\textsuperscript{88} and Johnson and Christy.\textsuperscript{89} The localized surface plasmon resonance redshifts by about 40 meV in the latter case.

**S4 Plasmonic mode decay**

In order to investigate saturation of the coupling strength in our seven-layer flake of WS\textsubscript{2} as was also observed by Stührenberg et al.\textsuperscript{10} in WSe\textsubscript{2}, we integrate the energy density of the field inside the WS\textsubscript{2} inside a cylinder with a radius of 20 nm around the nanodisk. The energy is then reported at the middle of each of the seven layers (i.e. 0.31 nm corresponds to the middle of the first layer, and 4.02 nm to the middle of the seventh). We expect the field energy to decay exponentially away from the nanoparticle, and as such we fit the relative field energy, normalised to the total integrated energy, to the expression $E_0 \exp(-x/l_{pl}) + E_b$, where $E_0 + E_b$ is the initial value, $l_{pl}$ is the decay length, and $E_b$ is the normalised asymptotic background energy far away from the nanodisk.

The result can be seen in Figure S13 with the normalised values $E_0 = 0.121 \pm 0.002$, $l_{pl} = 1.88 \pm 0.08$ nm, and $E_b = 0.096 \pm 0.002$. With an interlayer distance of 0.618 nm, we see with these values that the energy decays to $1/e$ around the fourth layer.

We can therefore conclude that additional layers beyond the seventh will only marginally increase the coupling strength.
Figure S13: Evolution of the energy in the multilayer WS\textsubscript{2} fitted with an exponentially decaying function. The energy is reported in the middle of each layer.
References


