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Dissociation of two-dimensional excitons in monolayer WSe$_2$

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Two-dimensional (2D) semiconducting materials are promising building blocks for optoelectronic applications, many of which require efficient dissociation of excitons into free electrons and holes. However, the strongly bound excitons arising from the enhanced Coulomb interaction in these monolayers suppresses the creation of free carriers. Here, we identify the main exciton dissociation mechanism through time and spectrally resolved photocurrent measurements in a monolayer WSe$_2$ p-n junction. We find that under static in-plane electric field, excitons dissociate at a rate corresponding to the one predicted for tunnel ionization of 2D Wannier–Mott excitons. This study is essential for understanding the photoreponse of 2D semiconductors and offers design rules for the realization of efficient photodetectors, valley dependent optoelectronics, and novel quantum coherent phases.
As Johan Stark first observed in hydrogen atoms\(^1\), applying an electric field on Coulomb-bound particles shifts their energy levels and eventually leads to their dissociation (Fig. 1a). In condensed matter physics, Wannier–Mott excitons display features analogous to those of hydrogen\(^2\), but with the crucial difference that they recombine if they are not dissociated. Thermal energy is usually sufficient to ionize excitons in 3D semiconductors owing to their small binding energy \(E_B\) (typically a few meV). In contrast, quantum confinement effects and reduced Coulomb screening in low-dimensional materials give rise to large exciton binding energy \((E_B > 100\) meV\)), which prevents thermal or spontaneous dissociation even at elevated temperatures and exciton densities.

In particular, monolayer transition metal dichalcogenides (TMDs) have aroused tremendous interest due to their unique optical properties governed by prominent excitonic features\(^3–6\) and spin- and valley dependent effects\(^7–11\). These 2D semiconductors provide an exciting testbed for probing the physics arising from many-body Coulomb interactions\(^6,12\). Recently, all-optical experiments have revealed a wealth of physical phenomena such as exciton\(^13,14\), trion\(^15,16\), and biexciton\(^17\) formation, bandgap renormalization\(^18\), exciton–exciton annihilation\(^19–23\) and optical Stark effect\(^7,11\). Exciton dissociation, on the other hand, can in principle be assessed through photocurrent measurements since photodetection current directly stems from the conversion of excitons into free carriers.

A large number of studies have investigated photodetection performances of 2D TMDs\(^26–29\) and demonstrated their potential as photodetectors and solar cells. However, it is still unclear which dissociation process can overcome the large exciton binding energy and lead to efficient photocurrent generation in these devices. Theoretical studies suggest that strong electric fields may provide the energy required to dissociate the excitons\(^25–32\), but the precise mechanism governing exciton dissociation in 2D TMDs remains to be experimentally investigated.

Here, we address this important issue by monitoring the exciton dissociation and subsequent transport of free carriers in a monolayer TMD \(p–n\) junction through spectrally and temporally resolved photocurrent measurements. Combining these two approaches allows us to assess and correlate two essential excitonic properties under static electric field, namely the Stark shift and the dissociation time. Further, we make use of the extreme thinness of 2D materials and their contamination-free assembly into heterostructures to reliably control the potential landscape experienced by the excitons. By placing the monolayer TMD in close proximity to metallic split gates, we can generate high in-plane electric fields and drive a photocurrent (PC). We find that at low field the photoresponse time of our device is limited by the rate at which excitons tunnel into the continuum through the potential barrier created by their binding energy, a process known as tunnel ionization (Fig. 1a). Tuning the electric field inside the \(p–n\) junction further allows us to disentangle various dynamical processes of excitons and free carriers and to identify the kinetic bottlenecks that govern the performance of TMD-based optoelectronic devices.

**Results**

**Device structure and characterization.** Figure 1b, c presents a schematic and optical micrograph of our lateral \(p–n\) junction.
device made by assembling exfoliated flakes on metallic split gates ($V_{G1}$ and $V_{G2}$) separated by 200 nm (see “Methods”). Few-layer graphite flakes placed on both ends of a monolayer WSe$_2$ flake serve as ambipolar electrical contacts that we use to apply a bias voltage $V_{B}$ and collect the photogenerated charges. The lateral graphite-WSe$_2$-graphite assembly is fully encapsulated in hexagonal boron nitride, typically 20 nm thick, which provides a clean and flat substrate. Three devices were measured (see Supplementary Note 1 and Supplementary Figs. 1–3), but unless otherwise specified, all measurements presented in the main text are obtained at room temperature from the device shown in Fig. 1c.

Tuning of bias and gate voltages allows us to finely control the in-plane electric field $F$. Finite-element and analytical calculations of the electric field distribution in our device (see Supplementary Note 2 and Supplementary Figs. 4–7) provide us with a precise estimate of $F$ and the electrostatic doping inside the WSe$_2$ (Fig. 1d). Applying gate voltages of opposite polarity ($V_{asym} = V_{G1} = V_{G2} = -10$ V) leads to the formation of a sharp $p$–$n$ junction (Fig. 1e) with an in-plane electric field reaching 21 V $\mu$m$^{-1}$ (Fig. 1d). The photoresponse that we observed at the junction (Fig. 1c) follows a photodiode-like behavior: PC is only generated in the $p$–$n$ or $n$–$p$ configuration (see Supplementary Fig. 1c) and can be increased by applying a reverse bias voltage (Fig. 1f).

Spectral response. We probe the absorption spectrum in the photoactive region by measuring the PC as a function of photon energy $h\nu$ at a constant laser power $P$ and in-plane electric field $F$. Figure 2a shows the responsivity (PC/P) spectra of a device similar to the one presented in Fig. 1c, measured at various $V_{B}$ and at low temperature ($T = 30$ K) in order to reduce thermal broadening. We observe a pronounced peak at a photon energy $h\nu = 1.73$ eV, corresponding to the A exciton, and a step-like increase around 1.87 eV. For increasing electric field, this step-like feature broadens and an additional shoulder appears at 1.83 eV.

To identify the various spectral features, we compare the experimental spectra with first-principles calculations. Figure 2b shows the calculated absorption spectra for different in-plane electric fields $F$ and at room temperature ($T = 30$ K) in order to reduce thermal broadening. We observe a pronounced peak at a photon energy $h\nu = 1.73$ eV, corresponding to the A exciton, and a step-like increase around 1.87 eV. For increasing electric field, this step-like feature broadens and an additional shoulder appears at 1.83 eV.

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bandgap. The calculated spectra for higher field reproduce remarkably well the field-induced increase of the sub-bandgap absorption observed experimentally. This is a manifestation of the Franz–Keldysh effect, which results from the leakage of the free electron and hole wave functions into the bandgap (inset of Fig. 2b). We note that our experimental value of $\Delta E$ agrees well with the one estimated from the diamagnetic shift of a monolayer WSe$_2$ encapsulated between silica and hBN.$^{35}$ Larger $\Delta E$ has been observed in SiO$_2$-supported WSe$_2$ samples$^{36-38}$, underlining the role of the dielectric environment on the excitonic properties.$^{39}$

Excitonic Stark effect. Turning our attention to the A exciton photocurrent peak, we observe a pronounced red-shift as $V_B$ (Fig. 2c) and $V_{\text{asym}}$ increase. We attribute this to the DC Stark effect. In first approximation, the Stark shift of a 1s exciton (without dipole moment) is given by $\Delta E = -\frac{1}{2} \alpha F^2$, where $\alpha$ is the in-plane polarizability. As shown in Fig. 2d, the A exciton energy shows a quadratic dependence with the maximum in-plane electric field $F_M$ calculated for different values of $V_{\text{asym}}$ and $V_B$ (Fig. 2e), yielding a polarizability of $\alpha = (1 \pm 0.2) \times 10^{-6}$ Dm/V$^2$. This shift matches well with the predicted polarizability of $\alpha = 9.4 \times 10^{-7}$ Dm/V for $E_B = 170$ meV, thus supporting our previous spectral analysis. Interestingly, we note that the measured in-plane polarizability is two order of magnitude larger than the out-of-plane value recently obtained in PL experiments.$^{40}$ This strong anisotropy confirms the 2D nature of the A exciton and demonstrates the advantage of using in-plane electric fields for controlling the optical properties of TMDs.$^{34}$

Photoresponse dynamics. Along with the Stark shift, the application of a large in-plane electric field shortens the lifetime of excitons, which eventually decay into free electrons and holes (Fig. 1a). We probe these decay dynamics by assessing the photoresponse time $\tau$ of the device with time-resolved photocurrent measurements (TRPC), banking on the nonlinear photoresponse of the WSe$_2$. Figure 3a, b shows the strong sublinear power dependence of the photocurrent (and the corresponding responsivity) under resonant pulsed optical excitation ($h\nu = 1.65$ eV, see “Methods”). Many physical processes may be responsible for or contribute to the observed sublinearity, including phase space filling$^{41}$ and dynamic screening effects (e.g., bandgap renormalization$^{38}$). These many-body effects become intricate as the exciton gas approaches the Mott transition$^{42}$. However, recent time-resolved spectroscopy$^{19,22}$ and photoluminescence$^{20,23}$ experiments indicate that in this exciton density regime ($10^{11} \lesssim N \lesssim 10^{13}$ cm$^{-2}$), exciton–exciton annihilation (EEA, or exciton Auger recombination) is the dominant decay process for excitons in TMD$^{24}$. To account for EEA in the rate equation governing the photocurrent we add a loss term that scales quadratically with the exciton density ($\gamma N^2$, where $\gamma$ is the EEA rate). Assuming that each pulse generates an initial exciton population $N_0$, this model yields PC $\propto \ln(1 + \gamma N_0)$, which reproduces well the observed sublinear photoresponse (black lines in Fig. 3a, b, see Supplementary Note 5). Moreover, the fits capture adequately the variation of the sublinear photoresponse with bias (Fig. 3a, b) and gate (Supplementary Fig. 10a) voltages, from which we extract the values of $1/\gamma$ (Fig. 3c). Hence, these nonlinear measurements already offer an indirect way to probe the photoresponse time.

In order to directly extract $\tau$, we resonantly excite A excitons in the $p-n$ junction with a pair of 200 fs-long laser pulses separated by a variable time delay $\Delta t$, for various values of $V_{\text{asym}}$ (Fig. 3d, e). Due to the sublinear power dependence, the photocurrent displays a symmetric dip when the two pulses coincide in time ($\Delta t = 0$). By extending our nonlinear photocurrent model to the case of two time-delayed pulses (see Supplementary Note 5 and Supplementary Fig. 10), we can show that the time dependence of this dip is dominated by an exponential time constant corresponding to the intrinsic photoresponse time $\tau$ of the device. The photoresponse rate $\Gamma = \frac{1}{\tau}$ is extracted from TRPC measurements at various values of $V_{\text{asym}}$ (Fig. 3d, e) and $V_B$ (see Supplementary Fig. 10d) and presented in Fig. 3c. We observe
that \( \Gamma \) increases markedly with gate and bias voltages, and remarkably follows the same trend as the values of \( 1/\tau_\text{f} \) obtained from the power dependence measurements. Comparing these two results, we obtain an EEA rate of \( \gamma = 0.05 \text{ cm}^2\text{s}^{-1} \) which is similar to those found in WSe\(_2\)\(^{19,23}\), MoS\(_2\)\(^{21,22}\), and WS\(_2\)\(^{20,25}\). We also note that the shortest response time we measure, \( \tau_f = 10 \pm 0.4 \text{ ps} \), translates into a bandwidth of \( f = 0.55/\tau_f \sim 50 \text{ GHz} \), which compares with the fastest responses measured in TMD-based photodetectors\(^{43,44}\).

**Discussion**

To directly address the exciton dissociation caused by the in-plane electric field \( F_\text{M} \), we examine the dependence of the photoresponse rate \( \Gamma \) on \( F_\text{M} \) at the \( p-n \) junction (Fig. 4a). Clearly, two regimes can be distinguished. The rapid increase of \( \Gamma \) with \( F_\text{M} \) is attributed to dissociation by tunnel ionization. We verify this by comparing the measured \( \Gamma \) to the calculated tunnel ionization rate \( \Gamma_{\text{tun}} \), obtained by introducing the complex scaling formalism in the 2D Wannier–Mott exciton model (see Supplementary Note 4 and Supplementary Table 1). According to this model, \( \Gamma_{\text{tun}} \) can be evaluated in first approximation by the product of the “attempt frequency”\(^{45}\), which scales with \( E_\text{B}/h \), and the exponential tunneling term \( \exp\left(-E_\text{B}/e_0 d F_\text{M}\right) \), where \( e_0 \) is the elementary charge, \( d \) is the exciton diameter, and \( h \) is the Planck constant. We find that the dependence of \( \Gamma \) at low field \( (F_\text{M} < 15 \text{ V \mu m}^{-1}) \) coincides well with the calculated dissociation rate of excitons with \( E_\text{B} = 170 \text{ meV} \), in agreement with our photocurrent spectroscopy analysis. More importantly, this shows that in the low-field regime the exciton dissociation process is the rate-limiting step governing the generation of photocurrent. We note that in multilayer TMDs, where \( E_\text{B} \sim 50 \text{ meV} \), the ionization rate is two orders of magnitude larger than in the monolayer case\(^{46}\), and hence this process was not found to limit the photoresponse rate of multilayer devices\(^{44}\).

At high electric field \( (F_\text{M} > 20 \text{ V \mu m}^{-1}) \), the photoresponse rate deviates from the dissociation rate-limited model and enters a new regime characterized by a more moderate increase of \( \Gamma \) with \( F_\text{M} \). The observed linear scaling of \( \Gamma(F_\text{M}) \) suggests that, in this regime, the photoresponse rate is limited by the drift-diffusive transport of free carriers out of the \( p-n \) junction. By considering a carrier drift velocity \( v_\text{drift} = \mu F_\text{M} \), we estimate that carriers generated in the center of the junction of length \( L = 200 \text{ nm} \) escape the junction at a rate \( \Gamma_{\text{drift}} = 2\mu F_\text{M}/L \). Comparing this simple expression (dotted line in Fig. 4a) to the measured \( \Gamma \) at high field, we find \( \mu \approx 4 \pm 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \), which is very similar to the room temperature field-effect mobility that we measure in our sample (\( \mu_{\text{FE}} \approx 3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \)).

A complete photocurrent model is achieved by introducing competing loss mechanisms caused by the radiative and non-radiative recombination of excitons (see Supplementary Note 6). Good agreement with the experimental data is obtained by considering the finite lifetime of excitons \( (\tau_{r,N} = 1/\Gamma_{r,N} \sim 30 \text{ ps}^{-1}) \) at zero electric field. This comprehensive picture of the dynamical processes (Fig. 4b) offers valuable insights into the internal quantum efficiency (IQE) of the photocurrent generation mechanism in this device. Indeed, the efficiency \( \eta \) of each
photocurrent step depends on the competition between the PC-generating ($\tau_{\text{drift}, \tau_{\text{diss}}}$) and the loss ($\tau_{\text{rec}}$, $n$) pathways, such that $\eta_{\text{diss}} = \eta_{\text{rec}} + \eta_{\text{diss}} / \tau_{\text{rec}} + \eta_{\text{diss}} / \tau_{\text{diss}}$. In the inset of Fig. 4a, we compare the IQE measured at low power as a function of $V_{\text{bi}}$ with the total extraction efficiency $\eta_{\text{extract}} = \eta_{\text{drift}} \tau_{\text{drift}}$ derived from the kinetic model shown in Fig. 4b. We find that $\eta_{\text{extract}}$ captures very well the bias dependence of the IQE, indicating that we correctly identified the relevant PC-generating processes. The field-independent discrepancy of 30% is attributed to the collection efficiency $\eta_{\text{coll}}$, which we define as the ratio between the number of excitons reaching the $p-n$ junction and the number of absorbed photons. This value coincides with our analysis of the measurements are performed using a Ti:sapphire laser (Thorlabs Octavius) with a laser beam is split into two arms and recombined using 50/50 beamsplitters. A 1.65 eV (FWHM $\Delta E = 0.07 \text{ eV}$), which corresponds to the A exciton absorption peak. The laser beam is split into two arms and recombined using 50/50 beamsplitters. A 1.65 eV (FWHM $\Delta E = 0.07 \text{ eV}$), which corresponds to the A exciton absorption peak.

In summary, our study offers a global understanding of the fundamental mechanisms governing the exciton dynamics and associated PC response in monolayer TMDs under in-plane electric field. We demonstrate that despite their large binding energy, photogenerated excitons can rapidly dissociate into free carriers via tunnel ionization, thereby outcompeting recombination processes. Importantly, this knowledge allows us to identify the main material properties that limit photocurrent generation in TMDs such as carrier mobility, exciton binding energy, and lifetime. This provides guidelines in terms of device design, material quality improvement, and Coulomb engineering of the van der Waals heterostructure to further improve the performances of TMD-based optoelectronics devices and develop their applications in valleytronics. We finally note that the observed Stark and Franz–Keldysh effects open up exciting opportunities for modulating light with 2D materials.47

Methods

Device fabrication. Exfoliated layers are assembled in a van der Waals heterostructure using the same technique as described in ref. 48. The monolayer of WSe$_2$ is identified by photoluminescence measurement (see Supplementary Note 1). The heterostructure is deposited onto metallic split gates (15 nm palladium) defined by electron-beam lithography on a degenerately doped silicon substrate covered with a 285-nm-thick SiO$_2$ layer. These graphite flakes are electrically connected by one-dimensional contacts made of Ti/Au (2/100 nm).

Photocurrent measurements. Photocurrent measurements are performed using a photocurrent scanning microscope setup, where a laser beam is focused by a microscope objective (Olympus LUCPlanFLN × 40) onto the device placed on a piezo-stage (Attocube ANC300). Photocurrent is measured with a preamplifier and a lock-in amplifier synchronized with a mechanical chopper. A supercontinuum laser (NKT Photonics SuperK Extreme), with a pulse duration of ~40 ps, repetition rate of 40 MHz and tunable wavelength (from 500 to 1500 nm) is employed to characterize the devices, perform photocurrent spectroscopy, and measure the photocurrent power dependence. Time-resolved photocurrent measurements are performed using a Ti:sapphire laser (Thoralbs Octavius) with ~200 fs pulses (at the sample), with a repetition rate of 85 MHz, and centered at $h\nu = 1.65 \text{ eV}$ (FWHM = 0.07 eV), which corresponds to the A exciton absorption peak. The laser beam is split into two arms and recombined using 50/50 beamsplitters. A mechanical chopper modulates the laser beam in one arm (pump), while the other arm (probe) has a motorized translation stage that allows for the generation of a computer-controlled time delay $\Delta t$ between the two pulses.

Data availability. The data that support the findings of this study are available from the corresponding author on request.

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Author contributions

M.M. conceived and designed the experiments under the supervision of F.H.L.K., M.M., D.D., and F.V. fabricated the samples. M.M. and F.V. carried out the experiments. M.M. performed the data analysis and discussed the results with F.H.L.K., F.V., and P.S. T.G.P. developed the Wannier–Mott exciton model. T.P.G, M.B.L., M.D., and V.I.F. performed the electrostatic calculations, and S.H., S.L., and K.S.T. performed the ab-initio calculations. K.W. and T.T. provided hBN crystals. M.M., F.V., P.S., and F.H.L.K. co-wrote the manuscript, with the participation of T.G.P. and K.S.T.

Additional information

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