Composite nanomaterials of semiconductors and noble metals as plasmonic photocatalysts

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Harnessing sunlight and storing the energy in chemical bonds is an important element in the transition towards green and sustainable technologies. Solar fuel production requires photocatalysts that (1) absorb large parts of the solar spectrum, (2) generate charges with significant lifetimes and appropriate energies, (3) catalyze relevant chemical transformations from abundant, low-energy starting materials, and (4) are stable under operating conditions. A new avenue within solar fuels involve plasmonic metal nanoparticles (PNPs). These materials have tunable optical properties, exciting catalytic behavior, and can be more stable under operating conditions. Composite photocatalysts of semiconductor nanoparticles (SNPs) and PNPs exploit broadly the solar spectrum, provide new catalytic routes and expand the scope of solar photocatalysis.

The newly initiated project aims at developing composite nanomaterials of SNPs and PNPs from mild, aqueous synthesis protocols and testing the catalytic properties of these plasmonic photocatalysts.

### ONE-POT SYNTHESIS AND CHARACTERIZATION OF ZnO-AuNP HYBRID

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<th>Step</th>
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<td>1.</td>
<td>CAPS buffer at pH 11</td>
<td>Heat to 95 °C</td>
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<td>2.</td>
<td>Add Zn precursor</td>
<td>Heat to 95 °C</td>
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<td>3.</td>
<td>Slowly add Au precursor</td>
<td>Heat to 95 °C</td>
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<td>4.</td>
<td>ZnO-Au hybrid</td>
<td>Final mixture is heated again reducing the Au precursor forming ZnO hybrids.</td>
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Composite nanomaterials of ZnO nanobipyramids tipped with anisotropic AuNPs were prepared under mild conditions in buffered aqueous solution in one pot by sequential precipitation of ZnO from Zn(OAc)₂ and deposition of gold by reduction of HAuCl₄.

The ZnO nanobipyramids have a measured band gap of 3.28 eV, as expected, and broad scattering in the visible. The addition of small (2 wt%) amounts of gold increased significantly the absorbance in the visible with a broad feature around 600 nm resulting in a colour change from white to purple. Transmission electron microscopy (TEM), scanning TEM (STEM) and elemental mapping by energy dispersive X-ray spectroscopy (STEM-EDS) reveals that ZnO grows to form 900 × 200 nm “nanobipyramids” and upon reduction of the Au precursor, anisotropic AuNPs of 20-50 nm are deposited on the ZnO surfaces. The base and tips of the nanobipyramids are made up of the polar <001> facets which may be a responsible for the slightly selective deposition of gold at the tips.

### NEXT STEP: PHOTOCATALYSIS

The setup shown above has been established and will be used for assessing the photocatalytic properties of the single component and hybrid nanomaterials. The fiber bundle tip is mounted in a collimating tube making the setup very flexible for use with other instrumentation. The estimated power output of the IR filtered beam is 300 mW.

### CONCLUSIONS and OUTLOOK

The results presented here mark the very beginning of this project. Initial SNP/PNP hybrids of ZnO and Au were prepared demonstrating the buffered one-pot approach. More uniform products will be the target of further optimization of the synthesis. The geometry of the hybrid may provide good separation of oxidation and reduction sites while charge conduction along the c axis provides charge separation. Apolar facets of ZnO are generally less active for photocatalysis but this might be overcome by the rough stepped surface of the nanobipyramids. This, and the influence of gold, will be probed using the described light delivery system coupled with other techniques such as GC-MS and electrochemistry for product analysis.

### ACKNOWLEDGEMENT

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**Scheme 1. Synthesis of ZnO and ZnO-Au hybrids.** N-cyclohexyl-3-amino-propionic-sulfonic acid (CAPS) buffer is adjusted to pH 11 and heated to 95 °C before addition of Zn precursor solution. After formation of ZnO, the mixture is cooled and HAuCl₄ is added dropwise. Finally, the mixture is heated again reducing the Au precursor forming ZnO hybrids.

**Figure 1.** Purified and dried nanopowder of pure ZnO (left) or ZnO-AuNP hybrid nanomaterial (right). The low loading of Au results in a drastic colour change.

**Figure 2.** (A) Extinction spectra of purified and redispersed nanomaterials in solution. (B) Reflectance spectrum of drop cast films on glass. (C) Powder X-ray diffraction (XRD) patterns of obtained powders. (D) Rietveld refinement of XRD patterns confirming a low Au loading of a few wt% and highly anisotropic ZnO.

**Figure 4.** - (A) Temperature change during white light illumination at different concentrations (optical density, OD). (B) Estimated heating power as function of AuNP concentration.

**Figure 5.** Plasmonic heating setup. The tungsten -halogen light is filtered (passing 315-710 nm), and focused onto the cuvette and temperature monitored above the illuminated area.

**Figure 6.** Spectral response of the focused, infrared-filtered beam.