

Supplementary Information (2 pages)

First demonstration of CdSe as a photocatalyst for hydrogen evolution from water under UV and visible light

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Experimental Section

Materials: Cadmium chloride was purchased from Baker and Adamson (>99% purity), selenium powder from Aldrich (99.999% purity), hexadecylamine from Acros (>90% purity), trioctylphosphine from Aldrich (technical grade, 90%), octylamine from Acros (>99% purity), carbon monoxide gas from Airgas (chemically pure grade), and sodium nitrite from EMD Chemicals (>97% purity). Water was purified by a Nanopure II system to a resistivity of >18 M Ω .

Synthesis of CdSe nanoribbons

The nanoribbons were synthesized according the published method by Joo et al.¹ The reaction scale was doubled and carried out in situ using a two-flask setup. The first flask was a 50 ml 3-neck flask and contained 0.707 g (8.95 mmol) of selenium powder. Then 10 ml of octylamine was added to the flask. The second flask was a 100 ml 3-neck flask and contained 0.552 g (2.42 mmol) of cadmium chloride. Then 20 ml of octylamine was added to the flask. Both flasks were closed with rubber septa, vented appropriately, and purged with nitrogen for 2 hours while stirring. The first flask was then slowly bubbled with carbon monoxide gas for four hours. Simultaneously, the second flask containing CdCl₂ was heated to 120°C using a hot oil bath. After two hours it was cooled to 70°C and the selenocarbamate solution from flask one was directly fed via a transfer needle under N₂. After the feed was complete, the solution was stirred at 70°C for one hour and cooled to room temperature. The solid dispersion was then washed with a 1% trioctylphosphine/ethanol solution and centrifuged. The supernatant was discarded and three more washings were performed, followed by a final wash with pure ethanol. The resulting bright yellow CdSe nanoribbon paste was collected and stored in dark conditions in a sealed flask. Unlike the published method, the CdSe paste was not dried further. It was determined that the paste was 10% wt CdSe.

Photocatalytic measurements

Photolysis experiments were carried out using a home-built low pressure Hg lamp irradiation system composed of four 175 W commercial mercury lamps that produced a quantum flux of 5.82×10^{-7} mol/s inside the reaction vessel (a 100 ml quartz flask) based on ferrioxalate actinometry.^{2, 3} Measurements under visible light were conducted with a longpass filter ($\lambda > 400$ nm) composed of a jacketed beaker that contained 1.0 M aqueous sodium nitrite. With the UV filter the quantum flux in the reaction vessel was experimentally determined to be 1.80×10^{-8} mol/s. Gas samples

were analyzed with a Varian gas chromatograph using Ar carrier gas, a 60/80 Å molecular sieve column, and a thermal conductivity detector. For catalytic measurements about 10 mg of the ribbons were dispersed in 50 ml of de-ionized water (or 20% methanol/water, or 0.1M Na₂S:Na₂SO₃(aq)) in a 100 ml quartz flask. The mixture was degassed with three evacuation/Ar backfill cycles, backfilled with Ar to a pressure of ~600 torr, and irradiated for 5 hours while stirring. Samples for gas analysis were periodically removed using the attached gas chromatography system.

Characterization

TEM measurements were conducted on a Philips CM120 transmission electron microscope. Samples for TEM were deposited onto holey carbon-coated Cu grids and washed with ethanol before drying in 80°C oven for one hour. The lower resolution image (1 µm scale bar) was taken at 80 keV. The high resolution image (40 nm scales) was taken at 200 keV on a JEM-2500SE made by JEOL Ltd.

UV-vis and fluorescence spectra were collected on Ocean Optics DH2000 light source and HR2000 CG-UVNIR spectrometer, and a Yobin Ivon Fluoromax-P fluororimeter. Samples were prepared by diluting a small amount of CdSe paste in hexadecylamine (HDA)/chloroform solution (5% wt).

Cadmium analysis was performed using a Varian SpectrAA-220FS atomic absorption spectrometer. Samples were obtained from by filtering post irradiation catalyst dispersions with a 0.2µm filter prior to analysis. The instrument was calibrated with aqueous cadmium chloride standards made from experimental starting material.

The details of the transient absorption spectrometer have been described previously.³ Excitation pulses of 70 fs duration and 400 nm were generated by SHG in a 1-mm BBO crystal. Pump and probe beams were defocused to 1mm to compensate for sample inhomogeneity and the pump fluence was ~20 mJ/cm². Samples were flowed through a 0.8 mm custom quartz cell. A 20 mL sample reservoir was used to prevent photodegradation and the reservoir was continuously sonicated during the experiment to minimize aggregation.

References

1. Joo, J.; Son, J. S.; Kwon, S. G.; Yu, J. H.; Hyeon, T., *J. Am. Chem. Soc.* **2006**, 128, (17), 5632-5633.
2. Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R., *Pure Appl. Chem.* **2004**, 76, (12), 2105-2146.
3. Compton, O. C.; Carroll, E. C.; Kim, J. Y.; Larsen, D. S.; Osterloh, F. E., *J. Phys. Chem. C* **2007**, 111, (40), 14589 -14592.