Supporting Information

Promoting photocatalytic multiple-electron reduction in aerobic solutions by Au-tipped CdSe nanorod clusters

Zheng Li, ^a Yongxing Hu,^a and Yugang Sun*^a

^{*a*} Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439 USA. Fax: +1-630-252-4646; E-mail: ygsun@anl.gov

Experimental details:

Chemicals: Trioctylphosphine oxide (TOPO, 99%, Aldrich), trioctylphosphine (TOP, 90%, Aldrich), cadmium oxide (CdO, 99.998%, Alfa), selenium (Se, 99.99%, Strem), didodecyldimethylammonium bromide (DDAB, >97%, Aldrich), dodecylamine (DDA, 98%, Aldrich), hexylphosphonic acid (HPA, 95%, Aldrich), dodecanethiol (>98%, Aldrich), n-tetradecylphosphonic acid (TDPA, PCI synthesis), gold (III) chloride (AuCl₃, 99.9%, Strem), 11-mercaptoundecanoic acid (MUA, 95%, Aldrich), methanol (MeOH, Fisher), ethanol (EtOH, Fisher), isopropanol (Fisher), toluene (Aldrich), chloroformx (CHCl₃, Fisher), potassium hydroxide (KOH, Mallinckrodt), methylene blue (MB, Aldrich) were used as received without further purification.

Synthesis of CdSe nanorods: 0.710 g TDPA, 0.160 g HPA, 3 g TOPO, and 0.200 g CdO were mixed and bubbled with nitrogen flow for 10 minutes at room temperature, and additional 10 minutes at 120 °C. The temperature of the solution was increased to and maintained at 300 °C under nitrogen blanket. 1.80 mL TOP was then swiftly injected to the solution after the CdO precursor was completely dissolved. In the next step, a solution of 0.073 g Se dissolved in 0.50 mLTOP was injected to the CdO solution at 300 °C to trigger the growth of CdSe nanorods. The reaction lasted for 6 minutes at 290 °C to complete the growth. The reaction solution was then cooled in air and 3 ml toluene was added at ~70 °C. After the solution was cooled down to room temperature, the solution was stored in the dark for further use.

Synthesis of Au-tipped CdSe nanorods: 0.0607 g AuCl₃, 0.1851 g DDAB, and 0.3429 g DDA were dissolved in 25 mL toluene with assistance of ultrasonication to form the gold precursor solution. 0.25 mL solution of the synthesized CdSe nanorods was processed by mixing it with 17.5 mL toluene and 7.5 mL isopropanol, followed by centrifugation at 8500 rpm for 5 minutes. After removal of the supernatant, the washing and centrifugation process was repeated one more time and the precipitated CdSe nanorods were re-dissolved in 20 mL toluene containing 0.9268 g DDA for the following step. 5 mL of the gold precursor solution was added dropwise to the toluene dispersion of CdSe nanorods within 2 minutes. The mixing simultaneously initiates the deposition of Au nanocrystals on the ends of the CdSe nanorods. After the reaction continued for an additional 3 minutes, 2 mL isopropanol was added. The Au-tipped CdSe nanorods were then

collected through centrifugation at 3000 rpm for 5 minutes and re-dispersed in 2 mL toluene. The entire process was performed at room temperature.

Synthesis of HMS nanorod clusters: 1mL of the toluene dispersion of the Au-tipped CdSe nanorods synthesized in the previous step was mixed with 0.3 g HPA, 0.3037 g dodecanethiol, and 4 mL toluene, followed by bubbling with nitrogen for 10 minutes at room temperature. With the protection of nitrogen blanket, the dispersion was then heated to and maintained at 60 °C for 15 minutes. To this incubated dispersion was added 1 mL isopropanol, the resulting HMS nanorod clusters were then collected through centrifugation at 3000 rpm for 5 minutes and redispersed in 1 mL toluene.

Transferring the Au-tipped CdSe nanorods and HMS nanorod clusters to aqueous solution: The as-synthesized nanostructures dispersed in 1 mL toluene (as defined in the previous two steps) were purified one more time by adding 10 mL methanol and centrifugation at 6000 rpm for 5 minutes. The precipitates were collected and re-dispersed in a solution made of 1 mL CHCl₃, 0.01 g MUA, and 4 mL KOH aqueous solution (5 mg/mL). The nanostructures were immediately transferred to the water phase by shaking and vortexing the mixed solution. 2 mL CHCl₃ was then added to the dispersion to promote phase separation. The collected aqueous dispersion (containing nanostructures transferred from the organic phase) was mixed with 10 mL methanol and centrifuged at 6000 rpm for 5 minutes. The precipitates were re-dispersed in 2 mL deionized water for photocatalysis.

Evaluation of photocatalytic performance: A 150 W quartz cold halogen lamp (Fibre-lite A3000, Dolan-Jenner Industries) with emission of 400-850 nm was used as the light source. In a typical photocatalytic reaction, 2 mL aqueous dispersion of the as-synthesized nanostructures (prepared in the previous step) was mixed with 0.2 mL aqueous solution of 20 mg L⁻¹ MB and 0.55 mL ethanol. Incubating the mixture in the dark for 1 hour led to an equilibrium of the adsorption/desorption of MB molecules on the HMS nanostructures. The solution was then exposed to the lamp to initiate the photocatalytic reduction of MB molecules at room temperature. During the reaction, aliquots (~0.2 mL) were taken out with a syringe at different times and were used to monitor the variation of the concentration of MB. Each aliquot was centrifuged at 13 000 rpm for 2 min to separate the HMS nanostructures from the solution and the supernatant was characterized with ultraviolet–visible (UV-Vis) absorption spectroscopy.

The intensity of absorption peaks were used to calculate the corresponding concentrations of MB in the solution. Magnetic stirring (at \sim 300 rpm) was maintained throughout the entire reaction. A fan was used to maintain air flow around the reactor, avoiding unnecessary temperature increase in the solution.

The normalization on the amount of catalysts (i.e., the weight of Au-CdSe) was based on equally splitting one batch of Au-tipped CdSe nanorods into two portions. One portion was used for controlled polymerization to form HMS nanorod clusters. In this polymerization process there is no change of total mass of Au-CdSe (i.e., no new Au or CdSe were generated and the existing materials did not dissolve). Another portion of the Au-tipped CdSe nanorods and the as-synthesized HMS nanorod clusters were then transferred to aqueous solutions in parallel. The phase transfer process can reach efficiency of at least 98% as reported in literature, which makes the potential sample losses during the phase transfer process to be negligible. In addition, the optical absorption measurements of the leftover solutions did not show measurable signal of Au-CdSe. Moreover, the optical absorption measurements of the supernatants generated from centrifugation also did not show measurable signal indicating the existence of Au-CdSe. These results confirm that the weight of Au-CdSe hybrid materials in the two samples used in Figure 3 were essentially identical.

Polymerization of Au-tipped CdSe nanorods into HMS nanorod clusters decreases the Au surface areas due to the fusion of Au nanotips. If the number of active sites on the Au surface plays the dominating role in determining the reduction reaction rate, we should observe the decreased photocatalytic efficiency for the HMS nanorod clusters in comparison to the corresponding Au-tipped CdSe nanorods. However, the observations show that the HMS nanorod clusters exhibit significantly higher photocatalytic efficiency than the Au-tipped CdSe nanorods. The results indicate that the charge separation in the CdSe nanorods and simultaneous accumulation of energetic electrons in the Au tips represent the determining steps for the reduction reactions and the surface area of Au plays the less important role in determining the reaction rate. Therefore, it is reasonable to standardize the catalysts based on the weight of Au-CdSe (or CdSe) rather than the Au surfaces.

Characterization: Optical absorption spectra were recorded on a Varian Cary 50 scan spectrometer, using a quartz cuvette with a 2 mm optical path. Energy-dispersive X-ray

spectroscopy (EDX) and transmission electron microscopy (TEM) images were acquired on a JEOL 2010F(s) with 200 kV operation voltage.

References:

1. S. Tamang, 2011, Synthesis and functionalisation of near infrared emitting nanocrystals for biological imaging, Ph.D. Thesis, pp. 55.



Fig. S1 Absorption spectra of CdSe nanorods (green), Au-tipped CdSe nanorods (orange), and HMS nanorod clusters (blue). The spectra were normalized against the intensity at 400 nm.



Fig. S2 TEM image of Au-tipped CdSe nanorods taken over a large area.



Fig. S3 High-resolution TEM image of individual Au-tipped CdSe nanorods.



Fig. S4 TEM images of HMS nanorod clusters with the number of CdSe nanorods of 2 and 3.



Fig. S5 EDX spectrum of the HMS nanorod clusters, showing the strong signals from Au, Cd, and Se. The signal of Cu originates from the TEM grid.