Cu2ZnSnS4–Au Heterostructures: Toward Greener Chalcogenide-Based Photocatalysts

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Abstract
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Cu$_2$ZnSnS$_4$−Au Heterostructures: Toward Greener Chalcogenide-Based Photocatalysts

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ABSTRACT: Chalcogenide-based semiconductor—metal heterostructures are interesting catalysts for solar-to-chemical energy conversion, but current compositions are impractical due to the relative toxicity and/or scarcity of their constituent elements. To address these concerns, Cu$_2$ZnSnS$_4$ (CZTS) emerged as an interesting alternative to other chalcogenide-based semiconductors; however, the fabrication of CZTS-metal heterostructures remains unexplored. In this paper, we systematically explore four methods of synthesizing CZTS-Au heterostructures, specifically: reaction of CZTS nanorods with either a soluble molecular gold precursor (AuCl$_3$) or preformed gold (Au) nanoparticles, each under thermal (heating in the dark) or photochemical reaction conditions (350 nm lamp illumination at room temperature). We find that using AuCl$_3$ under thermal deposition conditions results in the most well-defined CZTS-Au heterostructures, containing >99% surface-bound 2.1 ± 0.5 nm Au islands along the whole length of the nanorod. These CZTS-Au heterostructures are photocatalytically active, reducing the model compound methylene blue upon irradiation much more effectively than bare CZTS nanorods. We also demonstrate the removal of Au from the CZTS-Au heterostructures by amalgamation. These results open up a new area of greener, CZTS-based photocatalysts for solar-to-chemical energy conversion.

INTRODUCTION

Semiconductor—metal hybrid heterostructures are ideal photocatalytic materials for the study of solar-to-chemical energy conversion. 1−13 Traditionally based on semiconductor oxides such as TiO$_2$, 14−17 the field of semiconductor—metal hybrids saw a resurgence with the advent of colloidal II−VI, III−V, and IV−VI semiconductor nanocrystals, particularly those made of cadmium and lead chalcogenides. 18−23 The semiconductor’s photocatalytic activity, selectivity, and stability greatly depend upon metal modification,24 and recent studies show that plasmonic effects even enable unprecedented switching and fine-tuning of overall photocatalytic behavior.27−29 In an effort to replace cadmium, lead and arsenic-containing semiconductors, Cu$_2$ZnSnS$_4$ or “CZTS” recently emerged as one of the photovoltaic materials of choice for solar-to-power energy conversion.30−32 Made of Earth abundant, widely distributed, and relatively biocompatible elements, and with a direct band gap of 1.5 eV, Cu$_2$ZnSnS$_4$ is an affordable, greener, and more sustainable alternative to cadmium and lead chalcogenides. However, the use of Cu$_2$ZnSnS$_4$ in photocatalytic semiconductor—metal heterostructures for solar-to-chemical energy conversion remains unexplored.33−35

Several reviews detail the fabrication and applications of low dimensional CZTS and CZTSe nanostructures. 36−41 Historically hindered by spontaneous phase segregation into binary and ternary impurities, colloidal CZTS nanocrystals are now accessible via solution-phase synthesis methods.42−47 Anisotropic CZTS nanocrystals (nanorods, nanospindles, nanowires) are particularly attractive in order to achieve better charge carrier mobility across grain boundaries in photovoltaic cells, as well as more efficient suppression of electron−hole pair recombination in photocatalytic devices. Two recent reports looked at the interplay between molecular precursor reactivity, precursor concentration, and the ability to make true quaternary anisotropic CZTS nanocrystals (CZTS nanorods).48,49

In this paper, we use wurtzite (hexagonal) phase CZTS nanorods as a template for the deposition of gold (Au) nanoparticles. More specifically, we learn to deposit Au on CZTS using both thermal and photochemical methods from either a molecular gold precursor or preformed Au nanoparticles. We then use the resulting semiconductor—metal CZTS-Au heterostructures for solar-to-chemical energy conversion using the photocatalytic reduction of methylene blue as a model reaction. Finally, we explore the removal or stripping of gold particles from CZTS-Au heterostructures via amalgamation. The results of this work will serve as a springboard from which to build other greener, cost-effective, and more active, stable, and selective semiconductor—metal hybrid heterostructures for solar-to-chemical energy conversion.

RESULTS AND DISCUSSION

Multiple Metal Modification Methods. As noted in the Introduction above, metal heterostructures can be conveniently synthesized by either thermal or photochemical methods. Photochemical methods,50−55 including whole flask lamp...
Illumination methods\(^{18}\) offer many advantages such as control over nanoparticle loading through fine-tuning of the illumination or “irradiation” time,\(^{56}\) high selectivity for surface-bound vs freestanding metal particles,\(^{18}\) and selectivity for deposition along the length vs the tip of anisotropic semiconductor particles (rods, wires).\(^{57–59}\) Further, we noted during our work with CdE-M heterostructures (E = S or Se, M = Pt, Pd, Au)\(^{18,26,27}\) that pre-existing metal nanoparticles, particularly those made of gold (Au), have a tendency to adhere to chalcogenide surfaces. We thus hypothesized that we could deposit Au on CZTS not only from molecular gold precursors, but also possibly starting from preformed Au nanoparticles, in each case through either thermal or photochemical conditions.

### Metal Deposition from a Molecular Precursor

We started using AuCl\(_3\) as a soluble molecular precursor under thermal metal deposition conditions (60 °C in the dark, see Methods). Transmission electron microscopy (TEM) showed that this thermal procedure leads to well-defined, monodisperse heterostructures with a homogeneous distribution of Au islands along the whole length of the CZTS nanorods (Figure 1a). The Au metal islands have an average size of 2.1 ± 0.5 nm (Table 1). The great majority of Au particles (>99%) are surface-bound, meaning that they are attached to the surface of the CZTS nanorods. There are on average 9 ± 2 Au metal islands per CZTS nanorod. Based on TEM measurements and within error, the original length (28 ± 3 nm) and diameter (8 ± 1 nm) or aspect ratio (3.5 ± 0.6) of the CZTS nanorods (Figure 1a) are unaffected upon thermal Au deposition from AuCl\(_3\) (Table 1).

The soluble AuCl\(_3\) molecular precursor becomes much more reactive and deposition less controlled under photochemical deposition conditions (RT ≈ 21–24 °C at 350 nm, see Table 1.

Table 1. Thermal and Photochemical Deposition of Au Nanoparticles on CZTS Nanorods.\(^{a}\)

<table>
<thead>
<tr>
<th>Au precursor</th>
<th>conditions(^{b})</th>
<th>Au diameter(^{a})</th>
<th>%Au bound(^{a})</th>
<th>#Au NP/rod(^{a})</th>
<th>CZTS length(^{a})</th>
<th>CZTS width(^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuCl(_3)</td>
<td>Dark, 60 °C</td>
<td>2.1 ± 0.5 nm</td>
<td>&gt;99%</td>
<td>9 ± 2</td>
<td>28 ± 3 nm</td>
<td>8 ± 1 nm</td>
</tr>
<tr>
<td>AuCl(_3)</td>
<td>350 nm, R.T.</td>
<td>8 ± 6 nm</td>
<td>&gt;99%</td>
<td>2 ± 1</td>
<td>27 ± 5 nm</td>
<td>6 ± 1 nm</td>
</tr>
<tr>
<td>Au NPs(^{c})</td>
<td>Dark, 60 °C</td>
<td>2.0 ± 4 nm</td>
<td>64%</td>
<td>2 ± 1</td>
<td>25 ± 3 nm</td>
<td>8 ± 1 nm</td>
</tr>
<tr>
<td>Au NPs(^{c})</td>
<td>350 nm, R.T.</td>
<td>2.4 ± 0.6 nm</td>
<td>87%</td>
<td>2 ± 1</td>
<td>26 ± 4 nm</td>
<td>8 ± 1 nm</td>
</tr>
</tbody>
</table>

\(^{a}\)Postdeposition data for the resulting CZTS-Au heterostructures. \(^{b}\)In all cases, the starting CZTS nanorods (before deposition) were 28 ± 3 nm long and 8 ± 1 nm wide (aspect ratio ~3.5). \(^{c}\)The starting Au nanoparticles (NPs) were 2.0 ± 0.4 nm in diameter. (see Methods for synthetic details).
that using AuCl$_3$ as the gold precursor consistently leads to deposition. The CZTS nanorods appear to be significantly aggregated after deposition. However, this difference is statistically insignificant within experimental error (Table 1).

**Metal Deposition from Preformed Au Nanoparticles.** We then attempted to use independently synthesized, preformed Au nanoparticles with a diameter of 2.0 ± 0.4 nm for the synthesis of CZTS-Au heterostructures (Figure 2b). After reaction with CZTS under thermal deposition conditions (60 °C in the dark), TEM shows that the mean Au nanoparticle size (2.0 ± 0.4 nm) remains similar to that of the preformed Au particles before reaction (Figure 1c). This is also comparable to the Au nanoparticle size obtained thermally from AuCl$_3$ above. However, in this case only 64% of Au particles are bound to the CZTS surface. Counting only surface-bound metal particles, there is an average of 2 ± 1 Au islands per nanorod (Table 1). There is no evidence of changes in the length or diameter of the CZTS nanorods upon Au deposition by this method.

Under photochemical deposition conditions (RT ≈ 21–24 °C at 350 nm), the reaction of preformed Au nanoparticles with CZTS nanorods also results in a mixture of freestanding and surface bound gold. The mean Au nanoparticle size remains unchanged at 2.4 ± 0.6 nm (Figure 1d). However, 87% of Au nanoparticles are now surface bound to the CZTS nanorods, an even higher percentage than that obtained thermally at 60 °C from preformed Au nanoparticles (Figure 1c). If only surface-bound metal particles are counted, there is an average of 2 ± 1 Au islands per nanorod (Table 1). As in the previous example, there is no evidence of changes in the length or diameter of CZTS nanorods upon Au deposition by this method. However, the CZTS nanorods appear to be significantly aggregated after deposition.

Scheme 1 summarizes all of our deposition results. We note that using AuCl$_3$ as the gold precursor consistently leads to higher, near-quantitative (100%) formation of surface bound Au nanoparticles, likely because of the lower activation energy required for heterogeneous (seeded) nucleation of Au on the CZTS surface vs homogeneous nucleation of free Au in solution. Using preformed Au nanoparticles as precursors consistently leads to a smaller percentage of surface bound Au particles (64–87%). This percentage is nevertheless significant, and clearly demonstrates that nanogold avidly sticks to the soft, chalcogenide CZTS surface. The degree of attachment of Au particles is higher when the reaction is carried out photochemically (87%) than when it is carried out thermally (64%). It may well be that under illumination, enough negative charging occurs (for example, through electron trapping at defects sites) to make the CZTS surface even more polarizable and thus softer, increasing its affinity toward Au. In our previous work on photodeposition of Pt and Pd on CdS$_x$Se$_{1-x}$, we showed that we could increase the number of surface-bound metal particles to near 100% by using a wavelength that selectively excites the semiconductor and not the metal precursor. This is difficult to achieve here because there is significant overlap between the absorption profiles of CZTS nanorods and the AuCl$_3$ and Au nanoparticle precursors (Figure 3a).

**Characterization of CZTS-Au Heterostructures.** Figure 3b displays representative optical absorption spectra for the CZTS and Au nanoparticle precursors and the synthesized CZTS-Au heterostructures. The CZTS nanorods and all CZTS-Au heterostructures share the typical semiconductor absorption
edge around 850–900 nm and a second blue shoulder at 700 nm. The plasmonic resonance absorption feature at 500 nm observed in the preformed Au nanoparticles becomes broader, weakens, and blue shifts to about 400 nm in the CZTS-Au heterostructures. Figure 4 shows powder X-ray diffraction (XRD) patterns of CZTS nanorods and CZTS-Au hybrids, along with standard reference patterns for both CZTS and Au. CZTS retains the previously reported wurtzite (hexagonal) structure (assumed to be similar to hexagonal ZnS), and Au particles the common fcc metal structure.

To further characterize the CZTS nanorods, Au nanoparticles, and CZTS-Au heterostructures, we used X-ray photoelectron spectroscopy (XPS) (Figure 5). Figure 5a shows the Cu 2p and Au 4f XPS spectral regions of these three different materials. The Cu 2p binding energies observed for CZTS nanorods are the same before and after Au deposition: 951.6 eV (2p1/2) and 931.8 eV (2p3/2) for CZTS vs 951.3 eV (2p1/2) and 931.6 eV (2p3/2) for CZTS-Au. This is an indication that the oxidation state of Cu is unaffected by the deposition process. Reported Cu(I) 2p binding energies are 952.4 eV (2p1/2) and 932.1 eV (2p3/2), while reported Cu(II) 2p binding energies are 952.3 eV (2p1/2) and 932.2 eV (2p3/2). Because of this significant overlap in the binding energy values reported for Cu(I) and Cu(II), it is difficult to say with absolute certainty what the Cu oxidation state is in these materials from XPS data alone; however, we assume this is Cu(I) based on the known composition and observed crystal structure of CZTS as measured by powder XRD.

As expected, the CZTS nanorods do not show any Au 4f peaks before metal deposition, whereas the preformed Au nanoparticles and CZTS-Au heterostructures show characteristic Au 4f peaks (Figure 5b). The Au 4f binding energies observed for CZTS-Au were 88.1 eV (4f5/2) and 84.3 eV (4f7/2), while those observed for Au nanoparticles were 87.6 eV (4f5/2) and 83.8 eV (4f7/2). Reported zerovalent, Au(0) 4f binding energies are 87.4–87.9 eV (4f5/2) and 83.7–84.0 eV (4f7/2), whereas reported Au(I) 4f values are 88.3 eV (4f5/2) and 84.6 eV (4f7/2); for Au(III), we could only find a single reported value of 87.7 eV for the 4f7/2 spin state. Thus, Au nanoparticles show XPS binding energies that clearly fall within the values reported for zerovalent gold. The values seen for CZTS-Au fall slightly outside this range; however, they are much closer in value to the range reported for zerovalent Au (0) than to Au(I). While this does not rule out that a smaller fraction Au(I) may be present, our experimental values are a strong indication that some metallic, zerovalent Au was deposited on the surface of the CZTS nanorods.

Photocatalytic Testing. The bulk band gap and valence and conduction energy levels of CZTS are similar to those of CdSe, a relatively better studied semiconductor with demonstrated photocatalytic activity (Figure 6). Previous reports showed that CdSe-Au hybrids can photocatalytically reduce methylene blue (M.B.) to the colorless product leucomethylene blue (L.B.).61–64 CZTS and CZTS-based heterostructures are therefore good catalyst candidates for this reaction, and we sought to use the reduction of methylene blue to test the...
photocatalytic activity of CZTS-Au hybrids. As a stoichiometric or "sacrificial" source of electrons, we chose to use an alcohol such as methanol. Reduction of methanol to formaldehyde occurs at a lower potential than the reduction of M.B. to L.B.; methanol cannot be expected to directly reduce M.B. (Figure 6). However, photogenerated electrons sitting in the conduction band of CZTS should have enough energy to reduce M.B., and photogenerated holes sitting in the valence band of CZTS should have enough energy to oxidize the sacrificial methanol donor, thus replenishing the electrons in the valence band of CZTS and regenerating the neutral ground state of the catalyst (Scheme 2).

Scheme 2. Photocatalytic Reduction of Methylene Blue to Leucomethylene Blue Over CZTS-Au Heterostructures Using an Alcohol as Sacrificial Electron Donor

Photoinduced charge separation normally results in transfer of one carrier (for example, electrons) onto the metal islands of semiconductor–metal heterostructures. Figure 6 shows the energy levels of various metals commonly used in semiconductor–metal heterostructures, such as Au, Pt, and Pd. From this diagram, it would appear that electrons sitting in any of these metals would never have enough energy to react with methylene blue. However, it is known and has been shown previously that the electrons transferred to small metal islands such as Au metal can significantly increase the electron density within the Au nanoparticles, shifting their Fermi level toward more negative potentials.65 This transfer of electrons to the metal continues until the Fermi level equilibrates with the conduction band edge of the semiconductor, in this case CZTS.64 This explains how electrons transferred to the Au metal from the CZTS semiconductor can have enough energy to reduce methylene blue (M.B.) to leucomethylene blue (L.B.).

Before running any photocatalytic tests and in order to select the best conditions for catalyzed methylene blue reduction, we carefully looked at the irradiance profiles of different lamps as well as the optical absorption spectra of methylene blue and CZTS-Au heterostructures. As shown in Figure 7a, the light emitted by our 420 nm lamps does not have enough energy to directly photoexcite methylene blue; however, it can easily photoexcite CZTS-based nanostructures such as CZTS-Au. Therefore, we decided to run our photocatalytic tests under 420 nm lamp illumination, as this prevents any uncatalyzed, direct reduction or other unwanted side-reactions of methylene blue.

Figure 7b shows optical absorption spectra of methylene blue solutions before and after photocatalytic tests used to probe the reactivity of CZTS-Au. Without a catalyst, the peak at $\lambda_{\text{max}} = 663$ attributed to methylene blue remains virtually unchanged after 10 min illumination with the 420 nm lamps. However, when CZTS-Au was present the peak intensity decreased by 47% (see Methods for details). This represents a significant reduction in the amount of methylene blue (Figure 8). When
the concentration of CZTS-Au was cut by 1/5, we saw a 17% conversion of methylene blue. Without metal islands on its surface, using CZTS alone only resulted in about 2% conversion. These data are consistent with the fact that noble metal islands on the surface of semiconductor nanocrystals greatly increase photocatalytic activity. Interestingly, the photocatalytic activity of CZTS-Au remained and in some cases even increased after storage in the dark for 60 days (not shown).

**Metal Removal By Amalgamation.** An interesting concept in nanochemistry is the ability not only to build and assemble nano building blocks into more complex edifices but also to break apart and disassemble higher order structures into their separate components. With this in mind, we sought to probe whether Au nanoparticle islands can be removed from the CZTS-Au heterostructures to produce gold-free CZTS nanorods. To this end, we treated CZTS-Au heterostructures with a very small amount of liquid mercury metal (Hg, see Methods). Powder XRD analysis shows that two distinct phases form as a consequence of this treatment, namely, a new solid HgAu amalgam, and wurtzite CZTS. Consecutive, selective centrifugation allows separation of these two phases, at least partially (Figure 8). The AuHg amalgam “crashes” or precipitates out of solution first. This AuHg amalgam is composed of large, 10–20 nm particles characterized by their very dark contrast in bright field TEM due to their high apparent atomic number (Z) compared to CZTS (Figure 8a). Likely due to their high affinity for soft surfaces, the AuHg amalgam particles remain bound to a few CZTS nanorods. After a couple of centrifugation cycles, wurtzite CZTS becomes the dominant phase observed by XRD and TEM, and the characteristic Au plasmon peak is no longer visible in the optical absorption spectrum (Figure 8b,c). All small Au particles or islands disappear in favor of larger AuHg ones upon amalgamation.

**CONCLUSIONS**

We explored the fabrication of CZTS-Au heterostructures by a variety of pathways utilizing both a molecular gold precursor (AuCl₃) and preformed Au nanoparticles under thermal and photochemical deposition conditions. The high degree of binding (64–87%) observed when using preformed Au nanoparticles demonstrated the high affinity of nanogold for the soft chalcogenide CZTS surface; however, this binding was incomplete. Using a molecular gold precursor consistently resulted in a higher degree of surface bound Au nanoparticles than using preformed Au nanoparticles. Further, our results show that thermal deposition with a molecular precursor leads to a more controlled reaction with a homogeneous distribution of similar-sized Au metal islands along the whole length of CZTS nanorods.

We also demonstrated that CZTS-Au heterostructures are active photocatalysts, able to reduce methylene blue upon irradiation in the presence of a sacrificial electron donor (terminal reductant). Our results indicate that CZTS-Au is a much more active catalyst than CZTS alone, showing the synergy that makes heterostructures capable of undergoing photoinduced charge separation so attractive. We showed that CZTS-Au heterostructures are fairly robust, maintaining photocatalytic activity even after 60 days of dark storage. Treatment of CZTS-Au with a small amount of Hg led to the removal of small Au metal islands on the surface of the CZTS nanorods. The resulting AuHg amalgam remained difficult to separate completely from CZTS; however, these results demonstrate a method for breaking down a heterostructure into its individual components. In summary, CZTS-metal heterostructures are accessible by a variety of synthetic
pathways, and show promise for potential applications in solar-to-chemical conversion.

**METHODS**

**Materials.** Copper(II) acetylacetonate (Cu(acac)_2, 99.99%), methylene blue (>92%), mercury (Hg, 99.99%), dodecylamine (98%), didodecyl(dimethyl)ammonium bromide (98%), 1-dodecanethiol (98%), tert-dodecanethiol (98.5%), trietylphosphate oxide (TOPO, 99%), and toluene (anhydrous, 99.8%) were purchased from Sigma-Aldrich. Zinc acetate dihydrate (Zn(OAc)_2·2H_2O, 98%), gold(III) chloride (99.9%), and hydrogen tetrachloroaurate hydrate (chloroauric acid hydrate or HAuCl_4·3H_2O, 98.9%) were purchased from Strem Chemicals. Tetra-n-octylammonium bromide (98%), sodium borohydride (99%), mercaptosuccinic acid (99%), and 1-octadecene (ODE, 90%) were purchased from Acros. Tin(IV) acetate (Sn(OAc)_4, 98%) and tetramethylammoniumhydroxide pentahydrate (98%) were purchased from Alfa Aesar. Materials were used as received.

**Synthesis of Precursor Particles.** Colloidal CZTS Nanorods. CZTS nanorods were prepared according to a previously reported literature procedure. In a typical synthesis, a mixture of 1-dodecylthiol (0.52 mmol) and tert-dodecylthiol (0.17 mmol) were injected into a stirring mixture of Cu(acac)_2 (0.17 mmol), Zn(OAc)_2·2H_2O (0.25 mmol), Sn(OAc)_4 (0.25 mmol), TOPO (1.75 mmol), and 1-octadecene (ODE, 5 mL) in a three-neck round-bottom (R.B.) flask while argon (Ar) at 120 °C. The solution was heated to 210 °C and kept at this temperature for 30 min. After cooling to room temperature (R.T.), the mixture was twice washed with a 1:1 mixture of acetone, ethanol, and methanol followed by centrifugation at 4500 rpm for 10 min. The product could be readily dispersible in toluene.

*Au Nanoparticles.* Au nanoparticles were prepared according to a previously reported literature procedure. In a typical synthesis, a mixture of chloroauric acid (96.0 mg, 0.283 mmol) was dissolved in deionized water (10 mL) and tetra-n-octylammonium bromide (736 mg, 1.35 mmol) was dissolved in toluene (27 mL). The two solutions were combined and stirred vigorously until the gold (brown material) transferred to the organic layer. 1-Dodecylthiol (60.5 mg, 0.299 mmol) was then added to the organic layer. A solution of sodium borohydride (131 mg, 3.45 mmol) in deionized water (8 mL) added slowly to the mixture while stirring, and stirring continued for 3 h. The organic phase was separated and concentrated under vacuum to a ~10 mL volume. This was washed three times by precipitating with ethanol (10 mL) followed by centrifugation at 4500 rpm for 10 min. The product could be readily dispersible in toluene.

**Synthesis of CZTS-Au Heterostructures.** CZTS Stock Solution. CZTS nanorods were dissolved in toluene to give an optical density (O.D.) of 1.2 at 800 nm. A 10 mL volume of this solution was degassed, refliled with dry argon, and stored in the dark for ≥12 h in a three-neck R.B. flask.

*From AuCl₃ Precursor.* Under a dry Ar atmosphere, AuCl₃ (12.0 mg, 0.04 mmol), dodecylamine (53.2 mg, 0.29 mmol), and didodecyl(dimethyl)ammonium bromide (38.0 mg, 0.08 mmol) were dissolved in anhydrous toluene (9 mL) and injected into the CZTS nanorod solution via syringe. Deposition was then carried out for 15 min by one of two routes: (1) Thermally in the dark, in an oil bath pre-equilibrated at 60 °C, or (2) photochemically, under 350 nm illumination at room temperature (RT, 21–24 °C) in a fan-cooled Rayonet photoreactor (Southern New England Ultraviolet Company, Branford, CT) containing a set of 16 side-on fluorescent lamps and equipped with an air-cooling fan. Nonvolatile products were separated by precipitation with a 1:1:1:1 mixture of acetonitrile, ethanol, methanol, and acetone followed by centrifugation. The product could be readily dispersible in toluene.

*From Au Nanoparticles.* Au nanoparticles (see above) were dissolved in toluene to give an OD of 0.07 at 520 nm and stored in the dark for ≥12 h. The Au nanoparticle solution was injected into the CZTS nanorod solution via syringe. The deposition reaction was then carried out for 3 h by one of two routes: (1) Thermally in the dark, in an oil bath pre-equilibrated at 60 °C, or (2) photochemically, under 350 nm illumination at RT in a fan-cooled Rayonet photoreactor containing a set of 16 side-on fluorescent lamps and equipped with an air-cooling fan. Nonvolatile products were separated by precipitation with a 1:1:1:1 mixture of acetonitrile, ethanol, methanol, and acetone followed by centrifugation. The product could be readily dispersible in toluene.

**Transfer of CZTS-Au to Water.** CZTS-Au was dissolved in toluene (5 mL) inside a vial. A solution of tetramethylammonium hydroxide pentahydrate (420 mg, 2.32 mmol) and mercaptosuccinic acid (70 mg, 0.466 mmol) in deionized water (5.0 mL) was added, and the mixture stirred in the dark overnight. The aqueous layer was separated and washed twice with a 1:1 mixture of acetone and methanol followed by centrifugation at 4500 rpm for 10 min. The product was readily dispersible in water.

**Photocatalytic Reduction of Methylene Blue.** Reduction of methylene blue was carried out inside an oven-dried quartz cuvette topped with a septum and cap. A typical reaction involved 2.5 mL of 2.4 × 10⁻³ M of methylene blue in a 1:6 v/v alcohol (methanol or ethanol) to deionized water solution. CZTS-Au (0.5 mL of an aqueous solution with an OD of 0.718 at 800 nm) was added to the mixture, degassed by sparging with dry Ar for 15 min, and placed under 420 nm illumination at RT in a fan-cooled Rayonet photoreactor containing a set of 16 side-on fluorescent lamps and equipped with an air-cooling fan.

*Au-Stripping.* 12 mL of CZTS-Au solution with an OD of 0.44 at 800 nm was placed in a glass vial. Mercury (Hg, 103 mg) was added, and the mixture stirred for 12 h in an oil bath pre-equilibrated at 60 °C. The nonmercury organic liquid fraction was collected with a pipet, and the nonvolatile products were separated by precipitation with a 1:1:1:1 mixture of acetonitrile, ethanol, methanol, and acetone followed by centrifugation.

**Characterization.** Optical absorption spectroscopy was measured with an Agilent 8453 UV–vis photodiode array spectrophotometer. Powder X-ray diffraction (XRD) was measured using Cu Ka radiation on a Rigaku Ultima U4 diffractometer. Transmission electron microscopy (TEM) was conducted on carbon-coated nickel grids using FEI Tecnai G2 F20 field emission scanning transmission electron microscope (STEM) at 200 kV (point-to-point resolution <0.25 nm, line-to-line resolution <0.10 nm). Elemental composition was characterized by energy-dispersive spectroscopy (EDS). Particle dimensions were measured manually or with ImageJ for >200 particles. Average sizes (diameters) are reported ± standard deviations. X-ray photoelectron spectroscopy (XPS) was collected on a Physical Electronics S500 Multitechnique system using a standard Al Ka source. Analysis spot size was 1 × 1 mm
and the sample was mounted on 2-sided tape (3M). The binding energy values were determined using C 1s at 284.8 eV as a reference.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


(13) Zhang, N.; Liu, S.; Xu, Y.-J. Recent Progress on Metal Core@semiconductor Shell Nanocomposites as a Promising Type of Photocatalyst. *Nanoscale* 2012, 4, 2227–2238.


