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Synthesis of PdS-CdSe@CdS-Au nanorods with asymmetric tips with improved H₂ production efficiency in water splitting and increased photostability



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ABSTRACT

Charge separation is a crucial problem in photocatalysis. We used a wet-chemical method to synthesize asymmetrically tipped PdS-CdSe-seeded CdS (CdSe@CdS)-Au nanorod (NR) heterostructures (HCs). In these HCs, electrons and holes are rapidly separated and transported to opposite ends of the NRs by internal electric fields. Their ultraviolet-visible absorption spectra showed strong electronic coupling between both tips and the CdS body. PdS-CdSe@CdS-Au achieved a H₂ production rate of ca. 1100 μmol in 5 h; this is two orders of magnitude greater than the rate achieved with Au-CdSe@CdS NRs with only one tip. PdS-CdSe@CdS-Au NRs can withstand 4 h of photoirradiation, compared to 1.5 h for CdSe@CdS NRs, indicating that the photostability of PdS-CdSe@CdS-Au is much better than that of CdS. The greatly improved photocatalytic activity and stability are attributed to efficient charge separation and rapid charge transport in the PdS-CdSe@CdS-Au HCs.

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Photocatalysts such as heterostructured photocatalysts have shown promise for use in environmental remediation and water splitting [1,2]. In heterostructured photocatalysts, which are produced by incorporating cocatalysts into narrow band gap semiconductors, the internal electric field that can build up at the interface can be used to rapidly break up electron/hole pairs, thereby enhancing the solar-to-fuel conversion efficiency [3]. Li et al. [4–6] reported that dual cocatalysts consisting of Pt and PdS on CdS achieved the highest quantum efficiency (93%) obtained to date in H₂ production by water splitting. Grätzel et al. [7] immobilized a molecular cocatalyst on Cu₂O to produce a photocathode for CO₂ reduction, effectively enhancing the solar-to-fuel conversion efficiency. Nanocrystalline semiconduc-

tors such as CdS have advantages such as controllable well-defined geometric structures, few body and surface defects, and large surface areas [8]. These have been widely studied in recent decades [9–11] but the precise synthesis of sophisticated CdS heterostructures (HCs) with controllable well-defined structures is still a challenge. CdS suffers from severe photo-erosion [12]. One strategy for tackling such problems is to deposit a protective layer of ultrathin carbon around CdS; this greatly improves the photocatalytic stability and activity [13]. Another strategy is to synthesize HCs such as PbSe-CdS [14], which can pull electrons/holes away from CdS; this protects CdS from photo-erosion and improves the photocatalytic activity. One-dimensional HCs with tipped materials,

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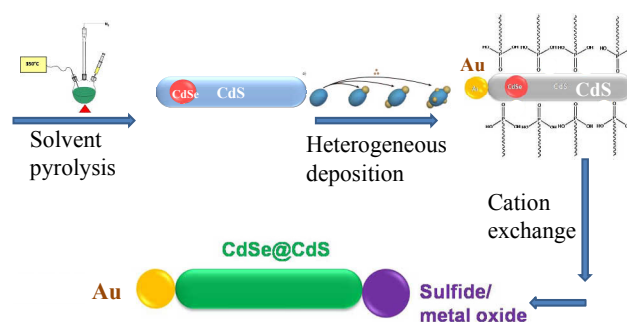
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such as Au-tipped CdSe-seeded CdS (CdSe@CdS) nanorods (NRs) are of particular interest because the long axis of the rod naturally provides a direct path for charge transport [15]. The production of such structures involves synthesis of semiconductor nanoparticles and subsequent heterogeneous nucleation and growth via a mild deposition process.

In our previous studies, we investigated the deposition of symmetric tips such as a metal (Au), metal oxide (Fe_3O_4), or sulfide (PdS) onto CdS NRs, i.e., the materials deposited on both ends of the NRs are the same [16]. In this process, it is necessary to minimize homogeneous nucleation of the metal precursor and/or Ostwald ripening of the semiconductor particles during deposition. Au-CdS NRs and PdS-CdS NRs show good charge separation [17]. Here, we report the deposition of asymmetric tips, i.e., one tip is Au and the other tip is PdS, on CdSe@CdS NRs. We used the obtained nanostructures in water splitting for H_2 production. The H_2 production efficiency and photocatalytic stability of CdS were greatly enhanced by efficient charge separation.

Scheme 1 shows the procedure for PdS-CdSe@CdS-Au NR synthesis. The synthesis of CdSe-seeded CdS NRs was described in detail in an earlier publication [18]. Au-tipped CdSe@CdS NRs with a match-stick structure were obtained by controlling the concentration of the Au precursor. In a typical synthesis, a HAuCl_4 solution (20 $\mu\text{g}/\text{mL}$, 2 mL) and a dodecylamine toluene solution (28 mg/mL, 2 mL) were mixed. A CdSe@CdS NR stock solution (~50 $\mu\text{mol}/\text{L}$, 1 mL) was injected into the mixed solution and the reaction was performed for ca. 30 min at room temperature. PdS was then deposited on the other end of the Au-CdSe@CdS NRs by cation exchange. A mixture of CdSe@CdS NR toluene solution (1 mL), oleylamine (2 mL), and oleic acid (1 mL) was rapidly injected into a $\text{Pd}(\text{acac})_2$ precursor solution at 180 $^\circ\text{C}$ and the reaction was continued for ca. 15 min under



Scheme 1. Schematic of synthetic procedures of PdS-CdSe@CdS-Au nanorod heterostructures via heterogeneous deposition and cation exchange methods.

N_2 . The product was transferred into an aqueous solution by ligand exchange with mercaptoundecanal acid and used for water splitting. An aqueous solution of the obtained photocatalyst (100 mL) was placed in a reactor under a 300 W Xe lamp. Na_2S (0.5 mol/L) and Na_2SO_3 (0.5 mol/L) were used as sacrificial reagents. The solution was thoroughly degassed and the amounts of H_2 evolved were determined by gas chromatography with Ar as the carrier gas.

Fig. 1 shows the structural characterization results for the as-synthesized CdSe@CdS NRs, Au-tipped CdSe@CdS NRs with a match-stick structure (Au-CdSe@CdS NRs), and asymmetrically tipped CdSe@CdS NRs (PdS-CdSe@CdS-Au NRs). The CdSe@CdS NRs are ca. 50 nm in length and 4.2 nm in diameter. The NR size is highly monodispersed. The transmission electron microscopy (TEM) image in Fig. 1(b) shows that round Au tips were deposited on one end of the CdSe@CdS NRs with a selectivity of ca. 85% by controlling the concentration of the Au precursor. The energy-filtered transmission electron microscopy (TEM) image in Fig. 1(c) confirms that the majority of the

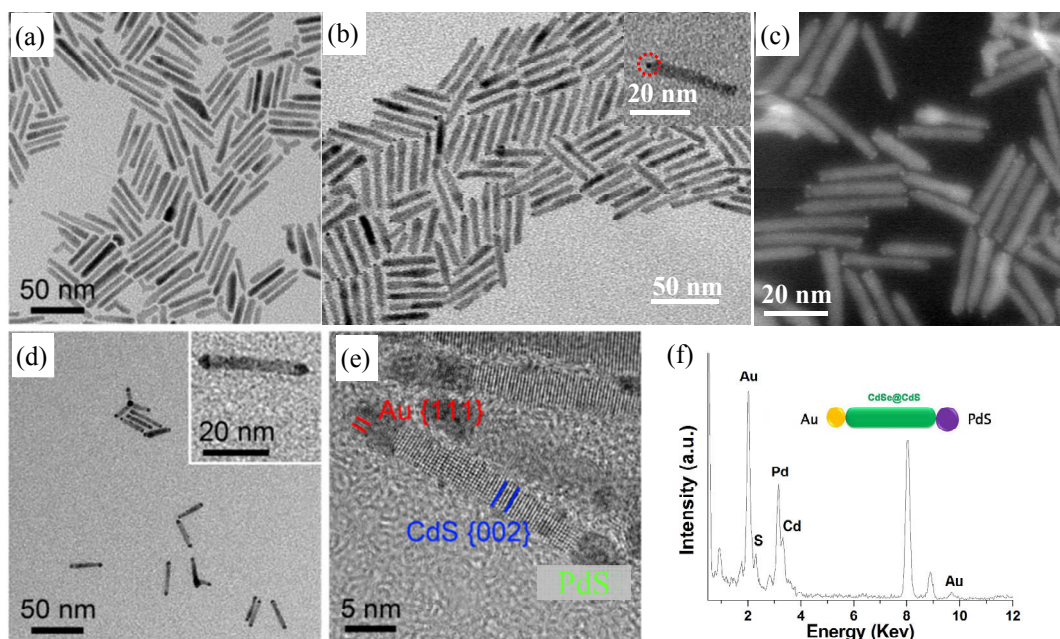


Fig. 1. TEM image (a) of CdSe@CdS nanorods; TEM image (b) and energy filtered STEM image (c) of Au-CdSe@CdS nanorods; TEM image (d), HRTEM image (e) and EDS spectra (f) of PdS-CdSe@CdS-Au nanorods. Inset images in Fig. 1(b) and (d) are magnification images of the corresponding samples.

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