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One-dimensional CdS@MoS$_2$ core-shell nanowires for boosted photocatalytic hydrogen evolution under visible light

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ABSTRACT

The well-defined one-dimensional (1D) CdS@MoS$_2$ (CM) core-shell nanowires are constructed by employing CdS nanowires (CdS NWs) as nanobuilding blocks via a facile hydrothermal strategy. The synergistic interaction, stemming from the large and intimate coaxial interfacial contact between MoS$_2$ thin shell and 1D CdS core, can efficiently retard the charge carrier recombination and the MoS$_2$ as noble-metal-free cocatalyst enriches the active sites for H$_2$ evolution from water. Consequently, in comparison to bare CdS nanowires, the resultant 1D core-shell CM composite exhibits distinctly enhanced visible light activity for the evolution of H$_2$. Notably, the activity of 1D CM with the optimized 2 wt% of MoS$_2$ exceeds that of pure CdS and CdS–1 wt% Pt composite by a factor of 64 and 4 times, respectively, under identical reaction conditions, while the apparent quantum yield (A.Q.Y.) at 420 nm over 1D CM reaches 28.5%. This work provides a simple paradigm for facile and finely controlled synthesis of well-shaped 1D-based composite photocatalysts towards boosted solar energy conversion.

1. Introduction

Splitting water into H$_2$ using semiconductor photocatalysts and solar energy has been regarded as a viable and sustainable solution with potential to address the increasing environmental and energy issues [1]. Since the first discovery of photo-electrochemical water splitting on a TiO$_2$ electrode [2], various photocatalysts have been extensively developed for H$_2$ production [3–10]. Among them, one-dimension (1D)-based semiconducting nanostructures, e.g., nanowires (NWs), nanorods (NRs) and nanotubes (NTs), have stirred mounting interests due to their intrinsic structural and electronic characteristics of large surface area with high length-to-diameter ratios, considerably higher electron mobility and vectorial electron transport with short radial distances [11–18]. For instance, very recently, Yu et al. have demonstrated that CdS NWs exhibit a higher photocatalytic H$_2$ evolution rate than its counterparts with other morphologies [19]. However, despite the fact that diverse 1D semiconductor photocatalysts have been constructed, almost no single one is able to impart efficient H$_2$ evolution activity even in the presence of sacrificial agent [20–23], which is still a critical obstacle to the wide practical application of 1D-based semiconductor photocatalysts.

To improve the photocatalytic activity for H$_2$ evolution, loading appropriate cocatalysts onto the surface of the photocatalysts has proven to be an effectual strategy [24–29]. In the hydrogen evolution reaction (HER), appropriate cocatalysts can significantly facilitate the reactions by synergistic effects of enriching the active sites, suppressing the charge recombination and reverse reactions, as well as lowering the activation energy [30–33]. Recent studies have demonstrated that MoS$_2$, a transition metal sulfide consisting of three atom layers (S-Mo-S) stacking together via weak van der Waals interaction, is in a position to perform as an efficient cocatalyst for H$_2$ production due to the existence of abundant active sites stemming from the sulfur edge [34–40]. Additionally, the merits of earth-abundance, low cost, and nontoxicity outline the great potential for its widespread application in future hydrogen economy [41–47]. It is, therefore, of considerable interest to develop 1D semiconductors-MoS$_2$ hybrid photocatalysts with high activity and good durability for photocatalytic H$_2$ production.

Herein, 1D CdS NWs are employed as nanoscale building blocks for the construction of 1D CdS NWs@MoS$_2$ (CM) hybrid photocatalyst due to its desirable band gap ($Eg \approx 2.40$ eV) for absorption of visible light and suitable conduction band edge positions for H$_2$ evolution. The resultant well-shaped 1D core-shell structure provides large and intimate coaxial interfacial contact between MoS$_2$

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thin shell and 1D CdS core, thus promoting the transfer of photogenerated electrons from semiconductor core to MoS_2 thin shell. The 1D CM composite exhibits distinctly enhanced photocatalytic activity in comparison with both CdS NWs and CdS-Pt composites, and the heterostructure with optimal loading amount exhibits a H_2 evolution rate of 493.1 $\mu mol\,h^{-1}$ with an apparent quantum yield (A.Q.Y.) of 28.5% at 420 nm. It is anticipated that this work could potentially provide a new stepping stone for designing well-shaped 1D-based hybrid photocatalysts with boosted performance toward targeting artificial photoredox applications.

2. Experimental section

2.1. Materials

Chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), including cadmium chloride ($CdCl_2{\cdot}2.5H_2O$), sodium diethyldithiocarbamate trihydrate ($C_5H_{10}NNaS_2{\cdot}3H_2O$), ethylenediamine ($C_2H_8N_2$), thioacetamide ($C_2H_5NS$), sodium molybdate ($Na_2MoO_4{\cdot}2H_2O$), potassium fericyanide ($K_3[Fe(CN)_6]$), potassium ferrocyanide ($K_4[Fe(CN)_6]$), potassium chloride (KCl) and N, N-dimethylflormamide (DMF). All materials were analytical grade and used as received without further purification. Deionized water was used throughout this study.

2.2. Materials synthesis

2.2.1. Fabrication of CdS NWs

Uniform CdS NWs were fabricated as in our previous researches [48,49]. The details were presented in the Supporting information (SI).

2.2.2. Construction of 1D CM core-shell nanowires

The 1D CM core-shell nanowires were prepared via a facile hydrothermal method [50,51]. Typically, a certain amount of thioacetamide (C_2H_5NS) and sodium molybdate ($Na_2MoO_4{\cdot}2H_2O$) were dissolved in 40 mL of DI water to form a transparent solution. Then, 50 mg of as-prepared CdS NWs were dispersed in the obtained solution by sonication for 5 min. After stirring for another 60 min, the suspension was transferred to a 50 mL Teflon-lined stainless steel autoclave and then heated in an electric oven at 473 K for 24 h. Subsequently, the products were separated by centrifugation and washed with deionized water and ethanol for three times, respectively, followed by drying at room temperature with a gentle stream of N_2. The theoretical weight percent of MoS_2 in the 1D CM core-shell nanowires were controlled to be 1, 2, 5 and 10 wt% by changing the amount of C_2H_5NS and $Na_2MoO_4{\cdot}2H_2O$, and were referred to as C1M, C2M, C5M, and C10M, respectively. For comparison, the various amounts of Pt as cocatalyst were loaded onto the surface of CdS NWs via an in situ photodeposition method using H_2PtCl_6 aqueous solutions as precursor. Analogously, the resultant CdS-Pt composites with various amounts of Pt were denoted as C0.5P, C1P, C2P, respectively. The pure MoS_2 powders were synthesized under the same conditions without the addition of CdS NWs.

2.3. Characterization

The powder X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance powder X-ray diffractometer (40 kV, 40 mA) using Ni-filtered Cu Kα radiation in the 2θ ranging from 10 to 80° at a scan rate of $0.02^\circ\,s^{-1}$. The optical properties of the samples were analyzed by UV–vis diffuse reflectance spectroscopy (DRS) using a UV–vis spectrophotometer (Cary 500, Varian Co.) in which $BaSO_4$ was employed as the internal reflectance standard. Field-emission scanning electron microscopy (FE-SEM) was used to determine the morphology of the samples on an FEI Nova NANOSEM 230 spectrophotometer. The transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL model JEM 2010 EX instrument at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific ESCA Lab250 spectrometer, and all of the binding energies were calibrated by the C 1s peak at 284.6 eV. Nitrogen (N_2) adsorption-desorption isotherms and the Brunauer-Emmett-Teller (BET) surface areas were determined at 77 K using Micromeritics ASAP2010 equipment. The photoluminescence (PL) spectra for solid samples were investigated on an Edinburgh FL/FS900 spectrophotometer with an excitation wavelength of 380 nm.

The photocurrent measurement was carried out on a BAS Epsilon workstation without bias and the electrolyte was 0.2 M aqueous Na_2SO_4 solution (pH = 6.8) without an additive. The visible light irradiation source was a 300 W Xe arc lamp system equipped with a UV-CUT filter ($\lambda > 420$ nm). The electrochemical impedance spectroscopy (EIS) measurements were performed in the presence of 5.0 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ by applying an ac voltage with 5 mV amplitude in a frequency range from 1 Hz to 85 kHz under open circuit potential conditions. The cathodic polarization curves were obtained using the linear sweep voltammetry (LSV) technique with a scan rate of $0.2\,mV\,s^{-1}$. The details of the preparation of electrodes are presented in the SI.

2.4. Photocatalytic H_2 production

The photocatalytic experiments were carried out in a Pyrex vessel, which was attached a closed gas-circulation and evacuation system. Photoreduction of H_2O to H_2 was performed by dispersing 20 mg of photocatalyst in an 80 mL aqueous solution containing 8 mL lactic acid as the sacrificial agent. The photocatalytic system was thoroughly degassed and irradiated by a 300 W Xe lamp with a UV-CUT filter to cut off light with a wavelength $\lambda < 420$ nm. A continuous magnetic stirrer was applied at the bottom of the reactor in order to keep the photocatalyst in suspension status during the whole experiment. The temperature of the reaction solution was maintained at 278 K by a flow of cooling water during the reaction. The evolved H_2 was in situ monitored periodically by an online gas chromatograph with a thermal conductivity detector (Shimadzu GC-8A, argon as a carrier gas and MS-5A column). The experimental set up is shown in Fig. S1.

The recycling test of catalytic H_2 evolution over the photocatalyst was done as follows. Typically, after the reaction of the first run under visible light irradiation, the photocatalytic system was thoroughly degassed again, without the separation of photocatalysts or the supplement of lactic acid. Subsequently, the thoroughly degassed system was irradiated again by a 300 W Xe lamp with a UV-CUT filter to cut off light with a wavelength $\lambda < 420$ nm. Analogously, the following three runs of photocatalytic recycling tests were performed.

The apparent quantum yield (A.Q.Y.) was measured under the same photocatalytic reaction condition and irradiated by a 300 W Xe lamp with a 420 nm band-pass filter (MIF-W, Optical Coatings Japan Co., Japan). The number of incident photons was measured using a radiant power energy meter (Ushio spectroradiometer, USR-40) The A.Q.Y. was calculated according to the equation below:

$$\text{A.Q.Y.\%} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\%$$
$$= \frac{\text{number of enolved hydrogen molecules} \times 2}{\text{number of incident photons}} \times 100\%$$