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Enhanced Photoelectrochemical Performance by a Direct Z-scheme CdO-CdS 1-Dimensional Nanorod Arrays

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Direct Z-scheme CdO-CdS 1-dimensional nanorod arrays were constructed through a facile and simple hydrothermal process. The structure, morphology, photoelectrochemical properties and H\textsubscript{2} evolution activity of this catalyst were investigated systematically. The morphology of the obtained nanorod is a regular hexagonal prism with 100–200 nm in diameter. The calcination temperature and time were optimized carefully to achieve the highest photoelectrochemical performance. The as-fabricated hybrid system achieved a photocurrent density up to 6.5 mA/cm\textsuperscript{2} and H\textsubscript{2} evolution rate of 240 mol/cm\textsuperscript{2}h at 0 V vs. Ag/AgCl, which is about 2-fold higher than that of the bare CdS nanorod arrays. The PEC performance exceeds those previously reported similar systems. A direct Z-scheme photocatalytic mechanism was proposed based on the structure and photoelectrochemical performance characterization results, which can well explain the high separation efficiency of photoinduced carriers and the excellent redox ability.

Key words: Direct Z-scheme, CdO-CdS, 1-Dimensional nanorod arrays, PEC performance, H\textsubscript{2} evolution rate

I. INTRODUCTION

The needs of energy are increasing rapidly due to the accretion of population and mushroom growth of the industry. Meanwhile, the increasing depletion of fossil energy and increasingly serious environment pollution make it one of the most urgent tasks to develop renewable and clean energy [1–3]. Since Fujishima and Honda [4] first reported the decomposition of water on TiO\textsubscript{2} electrode under illumination in an electrochemical cell, the concept of photoelectrochemical (PEC) water splitting has drawn great attention from researchers around the world. Due to the direct utilization of solar energy to split water into H\textsubscript{2} and O\textsubscript{2}, the PEC water splitting is a promising route to solve the energy and environmental crisis.

Over the last decades, numerous materials, such as Cu\textsubscript{2}O [5], TiO\textsubscript{2} [6, 7], BiVO\textsubscript{4} [8], ZnO [9], and WO\textsubscript{3} [10] have been reported as photocathodes or photoanodes in PEC cells for water splitting. Besides these, cadmium sulfide (CdS) has received much attention due to its visible light response ($E\textsubscript{g}$=2.4 eV) and suitable valence band (VB) and conduction band (CB) edges for overall water splitting [11–13]. However, the pure CdS is generally unstable and exhibits a low reactivity because of its serious inherent photocorrosion and rapid recombination rate of photogenerated carriers [14, 15]. Fabrication of a CdS-based heterostructure with other semiconductors is an efficient approach to overcome these problems [16–19]. Some successful examples, such as core-shell structured ZnO/CdS nanowire arrays [20], CdS/Cu\textsubscript{2}O/ZnO dual p-n junctions photoanode [21], and WO\textsubscript{3}/CdS nanowire arrays [22], have been reported to show enhanced PEC or photocatalytic reactivity and stability.

Similar to the heterojunction-type system, the Z-scheme composites have also attracted great interests because it not only improves the separation efficiency of the electron-hole pairs but also preserves excellent redox ability [23–26]. Cheng et al. [27] fabricated an all-solid-state CdS/An/ZnO ternary catalyst by depositing the An and CdS nanoparticles on the polar surface of ZnO crystals via a two-step self-assembly method. The ternary system showed the H\textsubscript{2} production rate was about 4.5 times higher than that of the binary CdS-ZnO. The An nanoparticles acted as an electron mediator to facilitate the efficient trans-
fer of photoinduced charges between CdS and ZnO via a Z-scheme mechanism. Tada et al. [28] constructed a Z-scheme CdS-Au-TiO$_2$ three-component nanojunction by the deposition-precipitation method. The system exhibited more than 2-fold higher photocatalytical activity for the methyl viologen reduction than that of the single- or two-component systems. The all-solid-state ternary Z-scheme structures generally use expensive precious metals, such as Au or Ag, as the electron mediators. Because of the surface plasmon resonance (SPR) effects, the noble metals can strongly absorb partial visible light, thereby reducing light absorption of photocatalysts. In addition, the controllable synthesis of ternary systems with desirable morphology and structure remains a challenge. So direct Z-scheme structures without electron mediators have also been exploited in recent years. Lu et al. [29] fabricated a direct Z-scheme TiO$_2$@CdS/CdO nanorod arrays by hydrothermal synthesis and successive ionic layer adsorption and reaction (SILAR). The sandwich structured systems achieved a photocurrent density of 3.2 mA/cm$^2$ at 1.23 V vs. RHE, about 141% higher than the CdS nanorod arrays. Cheng et al. [30] reported a direct Z-scheme TiO$_2$/CdS system by a simple SILAR method. The as-prepared hybrid photocatalyst showed remarkably enhanced photocatalytic H$_2$ evolution rate of 51.4 μmol/h.

Although there are several reported CdS-based direct Z-scheme systems, their PEC properties, especially the water splitting performance, have not been investigated in detail. The morphology and architecture of nanomaterials are well known to have significant impact on their PEC properties. Various CdS nanostructures, such as nanosphere [31], nanosheet [32], nanoparticle [33], and nanorod [34] have been reported. Among them, the vertically aligned 1-dimensional nanorod arrays with large aspect ratios would be more desirable because the 1-dimensional nanostructure not only enhances the light scattering and adsorption but also suppresses the recombination of photoinduced charges. For the fabrication of a direct Z-scheme structure, the intimate and sufficient contact interface between the two semiconductors is crucial for achieving efficient separation of photoinduced carriers. Despite many achievements, a simple and controllable method to fabricate a high-performance direct Z-scheme system is still needed. In this study, we fabricated successfully a 1-dimensional CdS-CdO direct Z-scheme nanorod array grown in-situ on FTO glass via a simple and facile hydrothermal reaction. The composite exhibited about 2-fold higher PEC performance and hydrogen evolution rate compared to the bare CdS nanorod arrays. The crystal structure, morphology, energy band structure, optical and PEC properties of the as-fabricated system were studied in detail by a series of characterization techniques. A direct Z-scheme mechanism was proposed to account for the enhanced PEC performance of the binary system.

II. EXPERIMENTS

A. Materials

Cadmium sulfate 8/3 hydrate (CdSO$_4$·8/3H$_2$O), Thiourea (CH$_4$N$_2$S), glutathione (C$_{10}$H$_7$N$_2$O$_6$S) were purchased from Sinopharm Chemical Reagent Co. Ltd. Fluorine-doped tin oxide (FTO, 2.0 cm×3.0 cm, 10 Ω/sq) glass was bought from Wuhan Lattice Solar Technology Co. Ltd. The FTO glass was cleaned by piranha solution (a typical mixture consists of 3 parts of concentrated sulfuric acid and 1 part of 30% hydrogen peroxide solution).

B. Preparation of CdS nanorod arrays

The CdS nanorod arrays were synthesized through a modified one-step hydrothermal method. CdSO$_4$·8/3H$_2$O was used as the cadmium source. In a typical procedure, 1.2 mmol CdSO$_4$·8/3H$_2$O, 1.2 mmol CH$_4$N$_2$S, 0.72 mmol glutathione and 40 mL ultrapure water (18.25 MΩ/cm) were mixed and transferred to a sealed Teflon-lined stainless-steel autoclave (50 mL) after thorough stirring. Then, the FTO glass was immersed into the mixed solution against the wall of Teflon-liner with conducting surface facing downwards. The hydrothermal reaction was performed at 473 K for 8 h and cooled to room temperature naturally. Finally, the obtained CdS nanorod arrays were rinsed several times with deionized water.

C. Fabrication of CdO-CdS nanorod arrays

CdO-CdS nanorod arrays were fabricated by calcining CdS nanorod arrays in air to form a CdO layer on the surface of CdS nanorods. The calcination conditions, including temperature and time, were optimized carefully to achieve the highest PEC performance. For comparison, the CdS nanorod arrays were annealed in Ar.

D. Catalyst characterization

The XRD patterns were collected with a Rigaku TTR-III equipped with Cu Kα radiation at 45 kV and 200 mA with a step length of 0.02° over a range of 10°–70°. The morphology of the arrays was examined by using the Schottky field emission scanning electron microscopy (FEI SIRION200). The TEM and HRTEM images were collected with FESEM (Nippon technology co JEM-2100F). The X-ray photoelectron spectroscopy spectra of the samples were measured by using X-ray photoelectron spectrometer (Thermo-VG Scientific ESCALAB 250).

E. Photoelectrochemical measurement

The photoelectrochemical performance was measured over a CHI electrochemical analyzer (CHI650E, CH Instrument Inc., Shanghai, China). The nanorod arrays (1.0 cm×1.0 cm) were served as a working electrode,
a Pt sheet (1.0 cm x 1.0 cm) and Ag/AgCl (saturated KCl) were utilized as a counter and a reference electrode, respectively. A 300 W Xe lamp (Beijing China Education Au-light Co., Ltd., Beijing, China) was used as the light source with an AM 1.5 G filter to obtain one sunlight intensity of 100 mW/cm² (measured by TENMARS solar power meter TM-207). A mixed 0.25 mol/L Na₂S and 0.35 mol/L Na₂SO₃ solution were used as the electrolyte (pH=12.5). The photoinduced linear sweep voltammetry (LSV) I-V curves were measured from −1.5 V to 0.2 V (vs. Ag/AgCl) with a scan rate of 0.01 V/s. Photocurrent-time (I-t) curves were acquired under chopped light irradiation conditions at an on/off interval of 20 s with an applied potential of 0 V vs. Ag/AgCl. Mott-Schottky (MS) curves were obtained under a potential range from −1.5 V to 0.2 V vs. Ag/AgCl with a frequency of 1 kHz, under dark conditions. The incident photon to current conversion efficiency (IPCE) was examined using a Zahner electrochemical workstation (IM6, Zahner Electrochemical Company, Germany) at 0 V vs. Ag/AgCl in a mixed 0.25 mol/L Na₂S and 0.35 mol/L Na₂SO₃ electrolyte solution. The IPCE at a given wavelength was calculated by the following equation [35]:

\[
\text{IPCE} = \frac{1240}{\lambda} \times \frac{(J_{\text{light}} - J_{\text{dark}})}{P_{\text{light}}} \times 100\%
\]

Where \(\lambda\) is the wavelength of the incident light, \(J_{\text{light}}\) and \(J_{\text{dark}}\) are the measured photocurrent and dark current density, respectively, and \(P_{\text{light}}\) is the light intensity at the specific measurement wavelength. Hydrogen evolution on the Pt sheet was evaluated in an air-tight Pyrex side-irradiation type reaction vessel connected to a closed gas circulation system (CEL-SPH2N, Beijing China Education Au-light Co., Ltd., Beijing, China) at 0 V vs. Ag/AgCl under AM 1.5 G illumination, and the H₂ production was measured on an on-line gas chromatography system (GC-7920, Beijing China Education Au-light Co., Ltd., Beijing, China) using a thermal conductivity detector.

III. RESULTS AND DISCUSSION

The crystal structure and phase of the prepared catalysts were verified by X-ray diffraction (XRD). As shown in FIG. 1, the XRD pattern of CdS nanorods calcined in Ar matches well with that of the wurtzite phase of CdS (JCPDS: 41-1049) except some peaks ascribed to FTO substrate. The main peak at the 2θ value of 26.5°, 36.6°, 47.8° can be attributed to the crystal planes of (002), (102), (103) of CdS, respectively. After calcination in air at 723 K for 90 min, no CdO diffraction peaks are detected, which can be attributed that the low amount of CdO formed on the CdS surface does not reach the detection limit of XRD. With prolonging the calcination time to 150 min or increasing the calcination temperature to 773 K, the new diffraction peaks at 33° and 55.26° appear (FIG. S1 in supplementary materials), which is assigned to the crystal facets of (111) and (220) of CdO (JCPDS: 05-0640), respectively.

FIG. 2 shows the SEM and HRTEM images of CdS nanorod arrays calcined in Ar and air, respectively. It is evident that the morphology of the ordered CdS nanorod arrays calcined in Ar is regular hexagonal prisms with smooth surface (FIG. 2(a)). Each hexagonal prism is about 100–200 nm in diameter. After calcination in air, the morphology and diameter of the nanorod arrays almost keep unchanged. However, the surface of the nanorod arrays becomes rough and there are irregular holes (FIG. 2(c)). The effects of different calcination conditions on the morphology of the samples are shown in FIG. S2 and S3 (supplementary material).
materials). Increasing the calcination temperature or the time results in a gradual agglomeration of the nanorods. The HRTEM images (FIG. 2 (b) and (d)) of the CdS nanorod arrays calcined in Ar and air further indicate that the lattice facet with a spacing of 0.32 nm corresponds to the (101) crystal facet of hexagonal CdS (FIG. 2(b)). The lattice fringes of 0.23 and 0.27 nm are consistent with the interplanar distances of (200) and (111) planes of CdO (JCPDS: 05-0640) (FIG. 2(d)), respectively. The EDS mapping image shows that the Cd, S, and O elements have a uniform distribution on the surface.

The surface chemical composition of the CdS nanorod arrays is analyzed by XPS technique. FIG. 3(a) shows the Cd 3d peaks of CdS nanorod arrays calcined in Ar and air, respectively. The sample calcined in air shows higher binding energies of Cd 3d$_{5/2}$ and Cd 3d$_{3/2}$ than that of the sample calcined in Ar, which is attributed to the formation of CdO [36, 37]. The reason is attributed that the electronegativity of oxygen is stronger than that of sulfur, thus the formation of Cd-O leads to a decrease of electron cloud density of Cd. Similar phenomenon is observed in the S 2p spectra (FIG. 3(b)). The binding energies of S 2p shift to higher values after calcination in air due to the surface oxidation [38]. All of the above observations implied that a layer of CdO was formed on the CdS surface after calcination in air.

For convenience, the CdS calcined in air is named as CdO-CdS in the rest of this article.

The PEC properties and water splitting activity of the fabricated CdO-CdS system were investigated in detail. FIG. 4(a) presents the transient light response and photocurrent density of the CdO-CdS and bare CdS nanorod arrays. The effects of calcination conditions on the PEC performance are shown in FIG. S4 and S5 (supplementary materials). The optimized calcination condition is 723 K and 90 min. It is obvious that when the light is on or off, the current shows an immediate response, which implies that the photocurrent is governed by the photons from the light. The photocurrent of CdO-CdS nanorod arrays reaches 6.5 mA/cm$^2$ at 0 V vs. Ag/AgCl, which is 2.1-fold higher as compared to the CdS (3 mA/cm$^2$). FIG. 4(b) shows the hydrogen evolution performance of the binary system at 0 V vs. Ag/AgCl. The hydrogen evolution rate of CdO-CdS reaches 240 μmol·cm$^{-2}$·h$^{-1}$, which is about 2-fold higher than the bare CdS nanorod arrays. To further quantify the photoresponse of these photoelectrodes, the IPCE of CdO-CdS and bare CdS were measured at 0 V vs. Ag/AgCl. As shown in FIG. 5, the IPCE value of CdO-CdS nanorod arrays at 365 nm reaches

FIG. 3 High-resolution XPS spectra of (a) Cd 3d and (b) S 2p.

FIG. 4 (a) I-t curves of CdO-CdS and CdS nanorod arrays at 0 V vs. Ag/AgCl under chopped AM 1.5 G illumination in a mixed 0.25 mol/L Na$_2$S and 0.35 mol/L Na$_2$SO$_3$ electrolyte solution. (b) The H$_2$ evolution rate plots of CdO-CdS and CdS nanorod arrays at 0 V vs. Ag/AgCl.
FIG. 5 IPCE curves of CdS calcined in air and Ar at 723 K for 90 min at 0 V vs. Ag/AgCl.

FIG. 6 The linear sweep voltammetry (LSV) curves of CdO-CdS and CdS nanorod arrays at a scan rate of 0.01 V s\(^{-1}\). The enhanced PEC performance could be ascribed to the formation of CdO layer on the surface of CdS nanorod arrays during calcination in air. FIG. S6 in supplementary materials shows the photocurrent stability test of the photoanode. After long time irradiation (4000 s), the photocurrent of the CdO-CdS nanorod arrays maintained nearly 80% of the initial value.

FIG. 6 depicts photocurrent density of the samples vs. applied potential under 100 mW/cm\(^2\) illumination. The linear sweep voltammetry (LSV) curves of these samples show negligible background currents under the dark situation. It is noted that the photocurrent onset potential of CdO-CdS nanorod arrays shifts to more negative value compared with CdS arrays. The more negative onset potential of CdO-CdS photoanode (FIG. 6(b)) suggests that the binary system has a stronger oxidizing ability. CdO is also an n-type semiconductor with a visible light response (\(E_g = 2.2\) eV). The CB and VB edges of CdO are more positive compared to CdS [39]. If the binary material conforms the type-II heterojunction mechanism, simultaneous light excitation of CdO and CdS will transfer the photoexcited electrons from CB of CdS to the more positive CB of CdO and photoexcited holes from VB of CdO to the more negative VB of CdS, which will reduce the redox ability. To further verify the possible mechanism, the Mott-Schottky plot was conducted to get the flat band potentials from the extrapolating of the linear portion of the plots. As shown in FIG. 7, the flat band of CdO-CdS negatively shifts to -0.95 V which means CdO-CdS has better reduction ability [40]. These results further demonstrate that the 1-dimensional CdO-CdS nanorod array fabricates an electron-mediator-free direct Z-scheme system (FIG. 8) rather than the type-II heterojunction mechanism. Both CdO and CdS can generate the electron-hole pairs under simulated solar irradiation. The photodiagram.
to induced electrons in the CB of CdO prefer to recombine with the holes in the VB of CdS. The leaving electrons accumulated in the CB of CdS contribute to the H2 evolution. This work provides a simple and facile route to fabricate an artificial direct Z-scheme system with excellent PEC performance for water splitting.

IV. CONCLUSION

In summary, 1-dimensional CdO-CdS nanorod arrays based on the electron-mediator free direct Z-scheme was successfully fabricated via a simple and facile hydrotherm method. The binary CdO-CdS system achieves a photocurrent density of 6.5 mA/cm2 and hydrogen evolution rate of 240 μmol·cm−2·h−1 at 0 V vs. Ag/AgCl, which is about 2-fold higher than that of the bare CdS nanorod arrays. 1-Dimensional nanostructure enhances the light harvest and suppresses the recombination of electron-hole pairs. The intimate interfacial contact between the CdS and CdO contributes to the fabrication of direct Z-scheme, which not only enhances the separation efficiency of photoinduced carriers, but also maintains the strong electron reduction ability.

Supplementary materials: Additional XRD, SEM and photoelectrochemical performance results in different calcination temperatures and time associated with this article can be found in the online version.

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