Enhanced photocatalytic H₂ production on CdS nanorod using cobalt-phosphate as oxidation cocatalyst

Tingmin Di, Bicheng Zhu, Jun Zhang, Bei Cheng, Jiaguo Yu

A State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, PR China
b Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

ABSTRACT

Employing visible light responsive semiconductor for photocatalytic hydrogen production by water splitting is an efficient way for utilizing renewable solar energy to solve the depletion of fossil fuel and environmental contamination. Herein, we report enhanced photocatalytic H₂-production performance over CdS nanorod using cobalt-phosphate (Co-Pi) as a water oxidation cocatalyst. The optimal Co-Pi modified CdS nanocomposite photocatalyst with the Co-Pi content of 8.4 mol% has a superior visible light H₂-production rate of 13.3 mmol h⁻¹ g⁻¹ with an apparent quantum efficiency of 24.3% at 420 nm, which is even higher than that of 1 wt% Pt-CdS (11.3 mmol h⁻¹ g⁻¹) under the same conditions. The enhanced visible-light photocatalytic H₂ production activity was attributed to the hole trapping and collecting ability of Co-Pi cocatalyst, which could effectively suppress the recombination of photogenerated electron-hole pairs and increase the electron density for hydrogen production. This work shows a possibility of using earth-abundant Co-Pi as cocatalyst for enhancing photocatalytic H₂ production.

1. Introduction

Considering the consuming of fossil fuel and growing of environmental pollution, hydrogen energy has attracted great interest because of its environmentally clean nature and high value of combustion. Photocatalytic hydrogen production from water splitting by solar irradiation is a promising approach for highly efficient hydrogen production [1]. Since Fujishima and Honda firstly reported photoelectrochemical water splitting on a TiO₂ electrode [2], many active photocatalytic semiconductors such as oxides, sulfides, and nitriles have been applied in photocatalytic water splitting [3–5]. While, most of the reported semiconductors can only harvest UV light, occupying only 4% of the sunlight energy. Therefore, it is very urgent to design and develop visible-light-responsive photocatalysts to efficiently utilize the solar energy. Due to the suitable band structure and excellent catalytic function, metal chalcogenides have received numerous attention in recent years [6–10]. In particular, CdS is regarded as one of the most effective visible-light photocatalysts for hydrogen evolution because of its narrow band gap (2.4 eV for bulk material) and sufficient conduction band overpotential for reduction of H⁺ to H₂ [11–17]. However, pristine CdS is not very active in hydrogen production in the absence of noble metal as cocatalyst due to the rapid recombination of photogenerated electron-hole pairs [18]. Also, these noble metals are too scarce and expensive [19,20]. Therefore, it is highly desirable to develop noble metal-free cocatalysts with high efficiency and low cost, such as nickel [21–24], copper [25] and cobalt [26,27] based materials.

Recently, cobalt-based oxides (CoO or Co₃O₄) have been extensively studied and proven to be effective oxygen evolution cocatalysts on several types of semiconductor photocatalysts [28–30]. In addition to cobalt oxides, cobalt-phosphate (Co-Pi) as an earth-abundant efficient oxygen evolving catalyst, reported firstly by Kanan and Nocera in 2008 [31], has been widely applied in photoelectrode devices [32–43]. The results suggest that Co-Pi can work as hole collector to reduce the recombination rate of electron-hole pairs and thus enhancing the efficiency. However, most of the reports mainly focus on the photoelectrochemical water oxidation for oxygen evolution, only few studies are about the photocatalytic water splitting for hydrogen production [44–46]. For example, Ge et al. reported the synthesis of Co-Pi modified graphitic carbon nitride (g-C₃N₄) photocatalysts via an in situ photodeposition method and the prepared samples showed higher photocatalytic activities for both O₂ and H₂ evolution than pure g-C₃N₄ [44]. Lee et al. also reported the enhanced photocatalytic water-splitting activity of graphitic-carbon-nitride in the presence of Co-Pi [45]. Herein, we for the first time reported the fabrication of Co-Pi/CdS nanorod composite photocatalyst via a simple photodeposition.
method and its superior visible-light photocatalytic H2 production activity. The H2-production activity of Co-Pi/CdS was even higher than that of Pt-CdS. Furthermore, a possible photocatalytic mechanism was proposed to explain the enhanced H2 production activity and strong stability.

2. Experimental

2.1. Sample preparation

All the reagents with analytical grade were used without further purification. Distilled water was used in whole experiments. Firstly, CdS nanorods were obtained by a solvothermal method. Typically, 12.5 mmol of Cd(NO3)2·2H2O and 37.5 mmol of thiourea were dissolved in 60 mL of ethylenediamine solution under stirring. Then the homogeneous solution was transferred to a 100 mL Teflon-lined autoclave and heated to 160 °C and kept at 160 °C for 24 h. After that, the yellow precipitate was collected by centrifugation and washed thoroughly with water and ethanol to remove dissolvable ionic impurities. Finally, the sample was dried at 80 °C in air.

Co-Pi cocatalyst was deposited on the surface of CdS nanorods by a simple photodeposition method as described previously [46]. Typically, 2 mmol of CdS nanorods were dispersed in 50 mL of phosphate buffer solution (0.2 M, pH = 7.0) prepared by NaH2PO4 and Na2HPO4 followed by ultrasonication. Subsequently, a specified volume of 0.02 M cobalt nitrate aqueous solution was added into the solution followed by UV light illumination (300 W Xenon lamp) for 3 h. After that, the sample was collected by centrifugation, washed with water and ethanol three times, respectively, and dried at 80 °C in air. The nominal atomic ratios of Co to Cd (designated as R) were 0, 1, 5, 10 and 20%, and the obtained samples were labeled as CC0, CC1, CC5, CC10 and CC20, respectively. Table 1 lists the actual chemical compositions of the prepared samples measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) using an Optima 4300 DV spectrometer (Perkin-Elmer). Pure cobalt phosphate was also prepared by mixing 0.5 M cobalt nitrate aqueous solution with phosphate buffer solution, and the obtained sample was labeled as C100. Furthermore, for comparison, the 1 wt% Pt loaded CdS nanorods sample (Pt-CdS, labeled CP1) was also prepared by photoreduction method using H2PtCl6 solution as the source of Pt.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained by a Rigaku X-ray diffractometer (Japan) using Cu Kα radiation. Morphological observations were conducted on a JEOL JSM-7500 field emission scanning electron microscope (FESEM, Japan). Transmission electron microscopy (TEM) analyses were conducted by a JEOL JEM-2100F electron microscope (Japan). UV–vis diffuse reflectance spectra were analyzed by a Shimadzu UV-2600 UV–vis spectrophotometer (Japan). The Brunauer–Emmett–Teller ( BET) specific surface area (SBET) of the powders was analyzed by nitrogen adsorption in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). The X-ray photoelectron spectroscopy (XPS) measurement was performed in a Thermo ESCALAB 250 XPS spectrometer system using Al Kα (1486.6 eV) radiation (operated at 150 W) in the constant analyzer energy mode with a 30 eV pass energy. The binding energies were referenced to the C 1s peak at 285.0 eV from adventitious carbon.

Table 1
Experimental condition for preparation of the samples and the corresponding physical properties.

<table>
<thead>
<tr>
<th>Samples</th>
<th>R (mol%)</th>
<th>Co (mol%) (ICP-AES)</th>
<th>SBET (m2 g⁻¹)</th>
<th>Pore volume (cm3 g⁻¹)</th>
<th>Activity (mmol h⁻¹ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC0</td>
<td>0</td>
<td>0</td>
<td>34</td>
<td>0.08</td>
<td>5.2</td>
</tr>
<tr>
<td>CC1</td>
<td>1</td>
<td>0.95</td>
<td>27</td>
<td>0.09</td>
<td>5.6</td>
</tr>
<tr>
<td>CC5</td>
<td>5</td>
<td>4.4</td>
<td>26</td>
<td>0.06</td>
<td>7.6</td>
</tr>
<tr>
<td>CC10</td>
<td>10</td>
<td>8.4</td>
<td>27</td>
<td>0.06</td>
<td>13.3</td>
</tr>
<tr>
<td>CC20</td>
<td>20</td>
<td>15.3</td>
<td>31</td>
<td>0.10</td>
<td>10.7</td>
</tr>
</tbody>
</table>

2.3. Photocatalytic performance

The photocatalytic H2 production experiments were performed in a 100 mL Pyrex flask at ambient temperature and atmospheric pressure according to our previously reported method. A 300 W Xenon arc lamp with a UV-cutoff filter (≥420 nm) was used as a visible-light source. In a typical photocatalytic H2 production experiment, 50 mg photocatalyst was dispersed in 80 mL lactic acid aqueous solution. Before irradiation, the suspension was bubbled with N2 for 30 min to remove the dissolved oxygen. During the photocatalytic experiments, a 0.4 mL gas was intermittently sampled from the flask, and H2 concentration was measured using a Shimadzu GC-14C gas chromatography (Japan) by thermal conductivity detector (TCD) method (5 Å molecular sieve column, nitrogen as carrier gas). The apparent quantum efficiency (QE) was measured under the same photocatalytic reaction conditions, except that four 420 nm LEDs (3 W) (Shenzhen LAMPLIC, China) were used as light source.

2.4. Photoelectrochemical measurements

Electrochemical analyzer (CHI660C, CHI, China) in a standard three-electrode system with the as-prepared samples as the working electrode, a Pt wire as the counter electrode and Ag/AgCl (saturated KCl) as a reference electrode, was used to perform the photoelectrochemical measurement. A 420 nm LED-light was utilized as the light source. Na2SO4 (0.5 M) aqueous solution was used as the electrolyte. The working electrodes were prepared as follows: 0.05 g of photocatalyst was ground with 0.5 mL of alcohol to make slurry. The slurry was then coated onto a 2 cm × 1.2 cm F-doped SnO2-coated glass (FTO glass) electrode by the doctor blade technique. Next, these electrodes were dried in an oven at 80 °C for 30 min. All investigated electrodes have a similar film thickness of 10–11 μm.

3. Results and discussion

3.1. Phase structure and morphology

The powder XRD was used to identify the phase structure of the prepared samples and investigate the influence of Co-Pi on the crystallinity of CdS nanorods. As illustrated in Fig. 1, for all the samples, the diffraction peaks can be easily indexed to hexagonal CdS (JCPDS NO. 06-0314). The peak position and intensity of these samples do not change much, implying that photodeposited Co-Pi cocatalyst has no significant influence on the phase structure and crystallinity of CdS nanorods. The diffraction peaks of pure Co-Pi (C100) are in good agreement with Co3(P04)2·8H2O (JCPDS NO. 33-0432), which is formed by the co-precipitation of Co2+ ions and phosphate anions. At low loading contents of Co-Pi cocatalyst (lower than 5 mol%), no obvious diffraction peaks of Co3(P04)2·8H2O was observed. This is because during the photodeposition of Co-Pi cocatalyst, low
concentration Co\(^{3+}\) ions were partially oxidized to Co\(^{4+}\) by the photogenerated holes from the valence band of CdS and amorphous Co-Pi compounds (CoPO\(_4\) or Co\(_3\)(PO\(_4\))\(_2\)) were formed [36]. In previous reports, the amorphous nature of Co-Pi has been fully proved on various semiconductors [43,46,47]. However, at higher concentration Co\(^{2+}\) (CC5, CC10, CC20 sample), exceeded Co\(^{3+}\) ions could not only be oxidized to form amorphous Co-Pi, but also precipitated with phosphate to form Co\(_3\)(PO\(_4\))\(_2\)-8H\(_2\)O crystal. Therefore, the diffraction peaks corresponding to Co\(_3\)(PO\(_4\))\(_2\)-8H\(_2\)O can be clearly observed for CC5, CC10, CC20 sample.

Fig. 2 displays typical SEM and TEM images of sample CC10 and its energy dispersive X-ray (EDX) pattern. As can be seen from Fig. 2a and c, the well-developed nanorod structure can be clearly observed, and the diameter of these CdS nanorods is about 20 nm. The HRTEM image (Fig. 2d) shows the crystal lattice fringes and the fringe with lattice spacing of ca. 0.336 nm corresponding to the (002) plane of hexagonal CdS [48]. Further observation shows that some small nanoparticles are deposited on the surface of CdS nanorods. Associated with the EDX result (EDX spectrum shown in Fig. 2b confirms the presence of Cd, S, Co, P and O element) and the discussion above, it can be concluded that these closely deposited clusters are amorphous Co-Pi. Moreover, the intimate contact between Co-Pi cocatalysts and CdS nanorods favors the transfer of photogenerated charge carriers, thus enhancing the separation of charge carriers and the enhancement of photocatalytic activity.

3.2. UV–vis analysis

Fig. 3 shows the UV–vis diffuse reflectance spectra of the prepared samples. The spectrum of CdS (CC0) shows intense absorption edge at around 520 nm, corresponding to a band gap of 2.4 eV [20]. For C100 sample, the absorption occurs at wavelength of 280 nm, while it has a wide absorption peak in the range from 400 to 750 nm due to the d–d transition of Co (II) [46,49]. After surface deposition of Co-Pi cocatalyst, the composites show a slight enhanced absorption in the visible-light region (520–750 nm) and the absorption slightly increases with increasing contents of Co-Pi (inset in Fig. 3). Moreover, no obvious absorption edge shift is observed in comparison with pure CdS, implying that Co-Pi cocatalysts were only deposited on the surface of CdS nanorods and not incorporated into the lattice of CdS.

3.3. XPS analysis

To further analyze the chemical status of elements of the prepared sample, XPS analysis was carried out. Fig. 4 presents the high-resolution XPS spectra of Cd 3d, S 2p, Co 2p and P 2p of sample CC10. The peaks of Cd 3d (Fig. 4a) located at 404.9 and 411.7 eV are ascribed to Cd 3d\(_{5/2}\) and Cd 3d\(_{3/2}\) of Cd\(^{2+}\), and the peaks of S...
2p (Fig. 4b) at 161.3 and 162.5 eV are associated with S 2p$_{3/2}$ and S 2p$_{1/2}$ of S$^2$-, indicating the presence of CdS [50]. In the case of P 2p (Fig. 4d), one single characteristic peak at 133.2 eV is indicative of P in phosphate group [38,47]. In Fig. 4c, two Co 2p peaks at 781.5 and 797.3 eV are assigned to the presence of Co$^{3+}$ [51]. The existence of Co$^{3+}$ explicitly suggests that Co$^{2+}$ was oxidized to Co$^{3+}$ in the photodeposition process and the Co-Pi cocatalysts were successfully deposited on CdS nanorods.

3.4. BET surface areas and pore size distributions

Fig. 5 depicts the nitrogen isotherms and corresponding pore size distributions (inset) of CC0 and CC10 samples. The nitrogen isotherms of the two samples belong to type IV according to the Brunauer–Deming–Deming–Teller (BDDT) classification, suggesting the presence of mesopores in the prepared samples [52]. The type-H3 hysteresis loop at P/P$_0$ of 0.7–1 discloses the existence of slit-like pores formed by the crossover and accumulation of CdS nanorods [48,53], which can be observed from SEM and TEM images in Fig. 2. The isotherms with high adsorption at P/P$_0$ = 1.0, suggest the samples with mesopores and macropores. Pore size distribution curves (inset in Fig. 5) indicate that two samples exhibit wide pore size distribution from 2 to 100 nm, also confirming the existence of mesopores and macropores. Table 1 gives the quantitative details on the BET surface area, pore volume and average pore size of the two samples. Compared with pure CdS (CC0), the BET surface area of the Co-Pi/CdS composites decreases slightly due to the surface deposition of amorphous Co-Pi cocatalyst.
3.5. Photocatalytic H2-production activity

In this work, hydrogen evolution of the samples was evaluated under visible light illumination (λ ≥ 420 nm) using lactic acid as sacrificial agent. The comparison of the photocatalytic H2 evolution rates of pristine CdS and Co-Pi/CdS composites was presented in Fig. 6. As can be seen, pure CdS nanorods show relatively low photocatalytic hydrogen production activity (5.2 mmol h⁻¹ g⁻¹) due to the rapid recombination of photogenerated electron-hole pairs and the fast backward reaction (recombination of hydrogen and oxygen into water). Notably, the deposition of Co-Pi cocatalyst on the surface of CdS nanorods enhances the hydrogen production rate, and the Co-Pi loading amount has a significant influence on the photocatalytic activity. With increasing the content of Co-Pi from 1 to 10 mol%, the H2 production rate of the composites gradually increases and achieves a maximum value of 13.3 mmol h⁻¹ g⁻¹ with an apparent quantum efficiency of 24.3% at 420 nm for the CC10 sample. Surprisingly, CC10 sample shows even higher H2 production activity than CdS nanorods loaded with optimal 1 wt% Pt, which is the most effective cocatalyst for photocatalytic H2 production due to its low overpotential and strong catalytic effect for H2 evolution [54]. Further increase in the content of Co-Pi leads to a decrease in the photocatalytic activity. This is related to the following factors: (i) high loading content of Co-Pi will cover the surface active sites of CdS nanorods and prevent the contact with water molecules; (ii) excessive loading of Co-Pi will shield the incident light and thus inhibit the light absorption and generation of electrons and holes of CdS nanorods; (iii) during the photodeposition, high Co²⁺ concentration results in the formation of Co₃(PO₄)₂ crystals, which will act as charge recombination centers, thus decreasing the photocatalytic activity. In addition, no hydrogen was detected when pure Co₃(PO₄)₂ was used as the photocatalyst, showing that Co₃(PO₄)₂ was not active for photocatalytic H2 production. Furthermore, the CC10 sample exhibited negligible decrease of activity after photocatalytic reaction for 12 h (Fig. 7). These results clearly demonstrate that Co-Pi was an efficient and stable cocatalyst for CdS to replace noble metals in photocatalytic hydrogen production.

3.6. Mechanism

Based on the above results and discussion, a possible photocatalytic H2 production mechanism over CdS nanorod with Co-Pi as oxidation cocatalyst under visible light irradiation was proposed and shown in Fig. 8. Firstly, during the photodeposition of Co-Pi cocatalyst, the valence band (VB) potential of CdS (1.88 V vs. NHE) is more positive than the oxidation potential of Co²⁺/Co³⁺ (0.7 V vs. NHE) [36,55]. Thus, the generated holes from VB of CdS can oxidize partial Co²⁺ to Co³⁺, resulting in the deposition of amorphous Co-Pi compounds (CoPO₄ and Co₂(PO₄)₂) on the surface of CdS nanorods. During the photocatalytic hydrogen production, the electrons are excited from the valence band to conduction band (CB) of CdS under visible light. Then H⁺ is reduced into hydrogen molecule on CdS surface by photogenerated electrons. Meanwhile, the holes in VB of CdS could transfer to the surface deposited Co-Pi cocatalyst, leading to Co³⁺ oxidized to Co⁴⁺. Further, lactic acid will obtain hole from Co³⁺ and is oxidized into pyruvic acid or CO₂ [56], meanwhile, Co⁴⁺ is reduced to Co²⁺ again (see Fig. 8) [35,57]. Therefore, not surprising, Co-Pi cocatalyst could function as an hole sink to assemble more holes from the VB of CdS and reduce the recombination rate of electron and hole. This is similar to the electron in CB of semiconductor transferring to metal [58–62].

3.7. Photoelectrochemical characterization

To further confirm the above suggested photocatalytic mechanism, transient photocurrent response and Mott–Schottky curves
were tested. The transient photocurrent response of CC0 and CC10 was recorded with four on–off cycles under intermittent light irradiation. As presented in Fig. 9, a considerable rise in the photocurrent response observed for the CC0 and CC10 samples indicates that the photogenerated electrons are rapidly produced and form photocurrent [63]. Two samples have a great anodic photocurrent spikes observed at the initial time of irradiation. After formation of the spike, a rapid decrease of the photocurrent with time is observed due to the recombination of the excessive holes with electrons [64]. It can be seen that the photocurrent of CC0 sample rapidly reaches constant after several seconds. However, the photocurrent of CC10 sample has a continuous decrease with time at the beginning, and then slightly increases. This is due to the deposition of surface Co-Pi, which could act as hole sinks and reduce the recombination of electrons and holes. Of course, it is easy to understand that the photocurrent value of sample CC10 is much higher than that of CC0 due to the presence of Co-Pi.

Mott–Schottky curve was used to characterize flat-band potentials (\(E_p\)) and free charge carrier density, which highly influence the photocatalytic activity of photocatalysts. As can be seen from Fig. 10, the positive slope of the curve suggests that CdS is an \(n\)-type semiconductor [65], and the deposition of Co-Pi on CdS nanorods does not alter the semiconductor nature of CdS. The flat-band potentials, calculated from the intercept of the liner plot with the horizontal axis, are \(-1.27\) and \(-1.12\) V vs. Ag/AgCl for CC0 and CC10 samples, respectively. The \(E_p\) of pure CdS agrees with other reported results [66,67]. The value of CC10 does not change much, implying that the Co-Pi deposited CdS has no great influence on the structure of CdS [30]. Further, the free charge carrier density was calculated according to Eq. (1):

\[
\frac{1}{C_{sc}} = \frac{2 \varepsilon \varepsilon_0 A^2 e N_{Dopant}}{\varepsilon_T A^2 (cm^2) \times \text{slope}(F^{-2} \times V^{-1})} (E - E_p - \frac{kT}{e})
\]

where \(C_{sc}\) is the capacitance of the space charge layer, \(\varepsilon_0\) is the vacuum permittivity, \(\varepsilon_T\) is the dielectric constant, \(A\) is the surface area, \(e\) is the electron charge, \(N_{Dopant}\) is electron donor density, \(T\) is the absolute temperature, \(F\) is the applied potential, and \(k\) is the Boltzmann constant. The x-intercept equals \(E_p + kT/e\) and the slope is proportional to the charge carrier concentration or doping density (\(N_{Dopant}\)) as shown by Eq. (2). This equation is obtained by substituting the relevant terms from Eq. (1).

\[
N_0 (cm^{-3}) = \frac{1.41 \times 10^{32} \times (cm \times F^{-2} \times V^{-1})}{\varepsilon_T \times A^2 (cm^2) \times \text{slope}(F^{-2} \times V^{-1})}
\]

The electron density of CC10 was calculated to be \(12.2 \times 10^{20} \, cm^{-3}\), higher than the \(8.6 \times 10^{20} \, cm^{-3}\) for CC0 sample, which is consistent with the \(H_2\)-production activity of the samples.

4. Conclusions

In summary, Co-Pi based oxidation cocatalyst was successfully deposited on the surface of CdS nanorods through a simple photochemical process in a neutral phosphate buffer solution containing \(Co^{2+}\) ions. The prepared Co-Pi/CdS composite samples exhibited excellent photocatalytic \(H_2\) production activity. The optimal 8.4 mol/Co-Pi modified CdS showed a 13.3 mmol h\(^{-1}\) g\(^{-1}\) visible-light \(H_2\)-production rate and an 24.3% \(H_2\)-production quantum efficiency at 420 nm, even higher than that of Pt-CdS sample under the same conditions. The surface deposited Co-Pi based oxidation cocatalyst can capture the holes from CdS, and reduce the recombination rates of photogenerated electron–hole pairs, thus obviously enhancing the hydrogen production activity of CdS. This study not only shows a possibility for replacing noble metal cocatalyst by earth-abundant Co-Pi for photocatalytic \(H_2\) evolution, but also provides new insight into design and fabrication of new \(H_2\)-production photocatalyst.

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