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Article

Zn_xCd_{1-x}S quantum dot with enhanced photocatalytic H₂-production performance

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ARTICLE INFO

Article history:

Received 7 March 2020

Accepted 24 April 2020

Published 5 January 2021

Keywords:

Zn_xCd_{1-x}S

Solid-solution photocatalyst

Photocatalytic H₂ production

Oil-soluble quantum dot

Water-oil soluble quantum dot

ABSTRACT

H₂ is an important energy carrier for replacing fossil fuel in the future due to its high energy density and environmental friendliness. As a sustainable H₂-generation method, photocatalytic H₂ production by water splitting has attracted much interest. Here, oil-soluble Zn_xCd_{1-x}S quantum dot (ZCS QD) with a uniform particle size distribution were prepared by a hot-injection method. However, no photocatalytic H₂-production activity was observed for the oil-soluble ZCS QD due to its hydrophobicity. Thus, the oil-soluble ZCS QD was converted into a water-soluble ZCS QD by a ligand-exchange method. The water-soluble ZCS QD exhibited excellent photocatalytic H₂-production performance in the presence of glycerin and Ni²⁺, with an apparent quantum efficiency of 15.9% under irradiation of 420 nm light. Further, the photocatalytic H₂-generation activity of the ZCS QD was ~10.7 times higher than that of the Zn_xCd_{1-x}S relative samples prepared by the conventional co-precipitation method. This work will inspire the design and fabrication of other semiconductor QD photocatalysts because QD exhibits excellent separation efficiency for photogenerated electron-hole pairs due to its small crystallite size.

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1. Introduction

With the consumption of fossil fuels, the problems of energy shortage and environmental pollution have become severe [1,2]. Alternative and clean energy sources, such as H₂ energy, should be developed. Photocatalytic H₂ production from water splitting by solar irradiation is a promising technology for solving the energy crisis and environmental pollution, and it can achieve solar-to-chemical energy conversion [3–6]. Photoelectrochemical water splitting on TiO₂ was reported by Fujishima and Honda [7]. TiO₂ has been extensively investigated

because of its high photocatalytic performance under UV-light irradiation. However, it utilizes only 4% of sunlight, thereby resulting in low utilization of sunlight, which restricts extensive practical applications [8–11]. Thus, researchers have studied visible-light response photocatalysts such as PbS [12], CdS [13–15], and CuInS₂ [16] that can utilize solar energy efficiently. Among these photocatalysts, CdS is a typical visible-light response photocatalyst that has been extensively investigated because of its narrow bandgap (2.4 eV) [17,18], negative conduction band (CB) position, efficient visible-light absorption, and sufficiently high reduction ability [19–21]. However, CdS

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This work was supported by the National Key R&D Program of China (2018YFB1502001), the National Natural Science Foundation of China (21871217, U1905215, 51961135303, 51932007, and U1705251), and the Innovative Research Funds of SKLWUT (2017-ZD-4).

DOI: 10.1016/S1872-2067(20)63614-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 42, No. 1, January 2021

suffers from severe photocorrosion, low separation, and low transfer efficiency of photogenerated carriers [22], which limit its extensive practical applications. To enhance the photocatalytic H_2 -production performance of the CdS photocatalyst, several strategies have been investigated, such as surface modification [23], heterojunction construction [24–30], and cocatalyst addition [21,31–35]. However, the current photocatalytic H_2 -production performance of CdS is still unsatisfactory. Thus, an effective method should be developed to further improve the photocatalytic H_2 -production performance of the CdS photocatalyst.

Utilizing solid-solution photocatalysts is one of the most promising strategies for enhancing the photocatalytic H_2 -production activity of CdS [36–38]. Generally, the bandgap and band edge position of solid-solution photocatalysts can be controlled by orbital hybridization [39]. Considering their broad light-adsorption properties, good dispersion in water, and effective charge transfer, colloidal QD semiconductor photocatalysts have been extensively studied [40]. In various QD photocatalysts, ternary chalcogenide nanocrystals, $Zn_xCd_{1-x}S$ QD (ZCS QD), have attracted widespread attention. ZCS QD has a controllable and appropriate bandgap, and a more negative CB position, thereby enhancing its photocatalytic H_2 -production performance [41]. Various strategies have been employed to prepare ZCS QD. For example, Yang et al. [42] prepared ZCS QD in an aqueous phase using $Zn(CH_3CO_2)_2$, $CdCl_2$ dehydrate, Na_2S as the reactant, and mercaptopropionic acid as the stabilizer at 100 °C for 90–120 min. Duan et al. [43] successfully synthesized hexagonal wurtzite structure ($ZnCdS$) nanocrystals by a solvothermal method at 150 °C for 1 h using dimethylsulfoxide as small molecular ligands. However, the QD obtained by these methods has a long reaction time, uneven particle size, strong aggregation, and a pungent smell. Thus, a ZCS QD photocatalyst with a small particle size and a uniform particle size distribution, which is beneficial for the transfer and separation of photogenerated electrons and holes, should be synthesized.

Here, an oil-soluble ZCS QD with a uniform particle size dis-

tribution was first synthesized according to the reported hot-injection method [44]. However, no H_2 -production activity was observed for the oil-soluble ZCS QD, because the H_2O molecule cannot directly contact QD. This indicates that the hydrophilic performance of QD is very important for photocatalytic H_2 production. Thus, converting the oil-soluble ligand into a water-soluble ligand by ligand exchange is an essential step for photocatalytic H_2 production, which can increase the hydrophilic properties of QD [45]. The ligand-exchange process of ZCS QD is shown in Fig. 1. Inorganic S acts as a hydrophilic surface ligand of ZCS QD, thereby resulting in QD with good hydrophilicity [40]. Considering its effective photogenerated carrier separation, broad visible-light absorption, small particle size, and hydrophilic surface inorganic S ligand, ZCS QD exhibits better photocatalytic H_2 -production performance than the $Zn_xCd_{1-x}S$ relative sample (ZCS RS). After the cocatalyst is added, the H_2 -production activity of the ZCS QD is further improved.

2. Materials and method

2.1. Synthesis of water-soluble ZCS QD

All the reagents were of analytical grade and were used without further purification. First, the oil-soluble ZCS QD was synthesized by the previously reported method [44]. Briefly, a mixture of 0.4 mmol CdO, 0.1 mmol ZnO, 15 mL of octadecene, and 1 mL of oleic acid was degassed for 20 min with N_2 , and heated to 130 °C for 20 min. After that, the mixed solution was further heated to 300 °C to obtain a clear colorless mixture solution of $Cd(OA)_2$ and $Zn(OA)_2$. At this temperature, 0.02 g of S powder dissolved in 3 mL of oleylamine was quickly injected into the mixture solution. The mixture solution was maintained at this temperature for 10 min.

After the solution was cooled to room temperature, approximately 10 mL of acetone was added to the solution for the precipitation of QD, and the supernatant was discarded. The precipitate was purified by dissolution in 1 mL of hexane and

Fig. 1. The schematic illustration of the ligand-exchange process for ZCS QD.

10 mL of acetone several times. The purified oil-soluble ZCS QD was added into a mixed solution containing 10 mL of hexamethylene and 10 mL of formamide solution with 2 g of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$. The mixed solution was stirred for 30 min to obtain water-soluble ZCS QD [46].

2.2. Synthesis of ZCS relative sample (ZCS RS)

ZCS RS was synthesized by the co-precipitation method. Typically, 0.1 mmol $\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$ and 0.4 mmol $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ were dissolved in 15 mL of H_2O with stirring for 10 min. After that, 0.5 mmol $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ was added into the mixed solution rapidly with continuous stirring for 30 min. The resulting sample was washed with water and ethanol to remove impurities. Finally, the product was dried at 60 °C in a vacuum.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded using a Rigaku X-ray diffractometer (Japan). Transmission electron microscopy (TEM) analyses were conducted on a JEOL JEM-2100F electron microscope (Japan). UV-vis diffuse reflectance spectra were obtained using a UV-2600 spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALA 250 instrument. The photoluminescence (PL) emission spectra were recorded on an F-7000 Fluorescence spectrophotometer. An FLS1000 fluorescence lifetime spectrophotometer (Edinburgh) was employed to record the time-resolved photoluminescence spectra (TRPL).

2.4. Photocatalytic H_2 -production performance test

The photocatalytic H_2 -generation experiments were performed in a 100 mL Pyrex flask at ambient temperature. Typically, 20 mg of the sample was dispersed in 80 mL of a solution containing 1 M glycerol and 20 μL (10 mg/mL) of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ solution. After the suspension was bubbled with N_2 for 30 min, the system was irradiated using a 300 W Xe arc lamp. Gas (0.4 mL) was intermittently sampled from the Pyrex flask, and the

concentration of H_2 production was analyzed by gas chromatography (GC-14C). The apparent quantum efficiency (AQE) was measured with four 420 nm LEDs in different directions.

2.5. Photoelectrochemical measurements

Electrochemical information was recorded on an electrochemical analyzer with a standard three-electrode system. The prepared sample, a Pt wire, and Ag/AgCl (saturated KCl) served as the working electrode, counter electrode, and reference electrode, respectively. Na_2SO_4 (0.5 M) was used as the electrolyte. The detail test condition of the Mott-Schottky measurement is as follows: the initial and final potentials are 0.4 and 1 V, respectively. The frequency and amplitude are 2000 Hz and 0.005 V, respectively.

3. Results and discussion

3.1. Phase structures and morphology

The crystal structure and morphology of the samples were respectively investigated by XRD and TEM. Fig. 2 shows the XRD patterns of ZCS QD and ZCS RS, together with the standard diffraction patterns of the cubic crystalline structure of CdS (JCPDS No. 75-1546) and the cubic crystalline structure of ZnS (JCPDS NO. 79-0043). ZCS QD and RS have similar XRD patterns. The diffraction peaks located at approximately 26.9°, 44.3°, and 52.4° can be indexed to the (111), (220), and (311) facets of the cubic-phase ZCS QD and ZCS RS. This result indicates that ZCS QD and ZCS RS have cubic crystalline structures [47,48]. Apparently, ZCS QD has broader peaks than ZCS RS. According to Scherrer's equation, the crystallite sizes of the ZCS QD and RS are about 4.2 and 7 nm, respectively. No impurity peaks are detected in the samples, thereby suggesting that the synthesized samples are of high purity. Zn^{2+} and Cd^{2+} have the same valence state, and the radius of Zn^{2+} (0.74 Å) is close to that of Cd^{2+} (0.97 Å). This result suggests that the solid-solution samples are easy to be synthesized [31].

The TEM image of the ZCS QD (Fig. 3a) shows that ZCS QD has a small particle size, which is in accordance with the XRD results. No agglomeration occurs in ZCS QD, which suggests that ZCS QD has good dispersion. The size distribution of ZCS QD further demonstrates that ZCS QD has a relatively uniform size of about 4 nm (inset of Fig. 3a). However, ZCS RS exhibits severe agglomeration (Fig. 3c). High-resolution TEM images of the ZCS QD (Fig. 3b) and RS (Fig. 3d) display crystal lattice fingers with a lattice spacing of 0.32 nm, which are indexed to the (111) plane of the cubic ZCS QD and RS [31]. According to the above results and analysis, the ZCS QD and RS were successfully synthesized by hot-injection and co-precipitation methods, respectively.

3.2. UV-vis diffuse reflection spectra and Mott-Schottky curves

The optical adsorption characteristics of the ZCS QD and RS were investigated by UV-vis diffuse reflection spectroscopy. The absorption edges of the ZCS QD and RS are located at about

Fig. 2. The XRD patterns of ZCS QD and ZCS RS.

Fig. 3. The TEM (a,c) and high-resolution TEM (b,d) images of ZCS QD (a,b) and ZCS RS (c,d).

496 and 590 nm, respectively (Fig. 4a). The absorption edge exhibits a blue shift at approximately 94 nm for ZCS QD, which is attributed to the quantum size effect of the ZCS QD. When the particle size drops to a certain value, the electron energy levels near the Fermi energy level change from quasi-continuous to discrete energy levels or the bandgap widens; this is referred to as the quantum size effect. According to the Kubelka-Munk

function, the bandgaps of the ZCS QD and RS are 2.5 and 2.1 eV, respectively (Fig. 4b). The ZCS QD has a higher bandgap than that of ZCS RS. The flat-band potentials of the ZCS QD and RS were analyzed by Mott-Schottky experiments (Figs. 4c and d). The Mott-Schottky plots have a positive slope, which is the typical characteristic of n-type semiconductors. The flat-band potentials of the ZCS QD and RS are obtained from the x-intercepts in the Mott-Schottky curves [49]. The flat-band potentials of the ZCS QD and RS could be approximately considered as the CB potentials [50]. Thus, the CB positions of the ZCS QD and RS are at -1.17 and -1.02 (V vs. Ag/AgCl at pH = 7), respectively. It can be deduced that the valence bands (VBs) of ZCS QD and ZCS RS are 1.33 and 1.08 (V vs. Ag/AgCl at pH = 7), respectively.

3.3. XPS analysis

The XPS spectra were obtained to further study the composition of surface elements and chemical valence states of the synthesized samples. The survey spectra show that no other elements are present, except for Zn, Cd, S, and C, thereby proving the existence of Zn, Cd, and S in the samples (Fig. 5a). The two characteristic peaks of Zn 2p are located at 1022.5 and 1045.6 eV, which are assigned to the binding energies of $2p_{3/2}$ and $2p_{1/2}$ of Zn^{2+} (Fig. 5b). The peaks of Cd 3d are located at 405.5 and 412.2 eV, corresponding to $3d_{5/2}$ and $3d_{3/2}$ of Cd^{2+} , respectively (Fig. 5c). S 2p is fitted into two peaks located at 162.1 and 163.5 eV (Fig. 5d), corresponding to $2p_{3/2}$ and $2p_{1/2}$ of S^{2-} , respectively, which are attributed to S combined with Zn and Cd [3,51]. The results agree with the XRD and TEM results. The high-resolution XPS results further confirm the existence of

Fig. 4. (a) UV-vis diffuse reflection spectra, (b) Kubelka-Munk function vs. photon energy curves, and Mott-Schottky plots of ZCS QD (c) and ZCS RS (d).

Fig. 5. (a) The survey spectra, (b) Zn 2p, (c) Cd 3d, (d) S 2p high-resolution XPS spectra of the ZCS QD and ZCS RS.

Zn, Cd, and S in the ZCS QD. At the same time, for ZCS RS, Zn, Cd, and S are also detected, as shown in the survey spectrum. Compared with the Zn 2p, Cd 3d, and S 2p peaks of the ZCS QD, the peaks of the three elements for ZCS RS shift slightly to low binding energies of 0.3, 0.2, and 0.4 eV, respectively, because of the different synthesis methods. However, the peaks still correspond to Zn^{2+} , Cd^{2+} , and S^{2-} . The above results and analysis further indicate that the ZCS QD and RS were synthesized successfully.

3.4. The separation and transfer of photogenerated carriers.

The steady-state PL emission and TRPL spectra of the ZCS QD and RS were measured to determine the efficiency of the photogenerated electron-hole pair separation, transfer, and recombination [52]. Fig. 6a shows the PL emission spectra of the ZCS QD and RS, with the excitation wavelength of 375 nm. PL emission peaks are generated by the irradiative recombination of the photogenerated electrons and holes [53]. The peak intensity of the ZCS QD is weaker than that of the ZCS RS, which indicates a low recombination rate of electron-hole pairs due to the small crystal size and the presence of inorganic S ligands on the surface of the ZCS QD [54]. The effect of surface inorganic S ligands is among the causes of the enhanced photocatalytic H_2 -production performance. The low recombination rate of electron-hole pairs can also be interpreted by TRPL spectra, as

shown in Fig. 6b. Fitted parameters are exhibited in Table 1. The average lifetime (τ_a) is calculated by the following formula: [55]

$$\tau_a = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2)/(A_1\tau_1 + A_2\tau_2 + A_3\tau_3),$$

where A_1 , A_2 , and A_3 refer to the pre-exponential factors; τ_1 , τ_2 , and τ_3 represent the fluorescence lifetimes during radiation, no radiation, and energy transfer. As shown in Table 1, the ZCS QD and RS exhibit similar irradiative lifetimes (τ_1). However, the percentage of the photogenerated carriers for ZCS QD (29.24%) is significantly lower than that for ZCS RS (65.38%). The average lifetime of the ZCS QD is higher than that of the ZCS RS, thereby demonstrating that the ZCS QD has a relatively low recombination rate of the photogenerated electrons and holes. The τ_2 and τ_3 of the photogenerated electrons for the ZCS QD are higher than those for the ZCS RS. At the same time, the percentages of the photogenerated carriers for the ZCS QD are significantly higher than those for the ZCS RS. This result demonstrates that these photogenerated carriers are likely to participate in photocatalytic reactions [53]. To study the separation, transfer, and recombination of the photogenerated carriers further, the transient photocurrent responses by several on-off cycles were measured under the same irradiation condition (Fig. 6c) [56]. The photocurrent intensity of the ZCS QD is distinctly higher than that of the ZCS RS, which indicates a higher separation and transfer efficiency of photogenerated carriers for the ZCS QD than for the ZCS RS. This result is in

Fig. 6. (a) Steady-state photoluminescence (PL), (b) time-resolved PL spectra, (c) transient photocurrent responses, and (d) electrochemical impedance spectroscopy (EIS) spectra of the ZCS QD and ZCS RS.

accordance with the PL and TRPL analysis results. The intensity of the photocurrent for the ZCS QD and RS shows no significant change after several on-off cycles. This result demonstrates that the photocurrent has satisfactory repeatability. Once the light is switched on, the photocurrent increases slowly before leveling off. This phenomenon occurs for the following reasons: The photogenerated electrons of the CB prefer to migrate to the surface traps of the samples and further to deeper traps. In this process, only partially photogenerated electrons can transfer to the electrode. Similarly, when the light is turned off, the trend of photocurrent decline is stable, thereby indicating that the surface traps can store electrons. The electrons are released gradually by the surface traps and migrate to the electrode [57]. The electrochemical impedance spectroscopy (EIS) spectra of the ZCS QD and RS were measured to determine the transfer efficiency of the photogenerated carriers (Fig. 6d). The semicircular radius corresponds to the charge-transfer impedance, which shows that the ZCS QD has a small semicircular radius. This result indicates a low charge-transfer resistance,

thereby leading to the fast transfer and separation of photo-generated carriers. This result is consistent with the above results. According to the above results and analysis, the ZCS QD has a high separation efficiency of the photogenerated electrons and holes, thereby resulting in enhanced photocatalytic H_2 -production activity.

3.5. Photocatalytic performance

The photocatalytic H_2 -production activities of the samples were evaluated based on the H_2 -production rate. The cocatalyst, Ni salts, was introduced into the photocatalytic H_2 -production solution, where glycerol was used as a sacrificial agent [58]. It should be noted that no photocatalytic H_2 -generated activity was observed for the oil-soluble ZCS QD in the presence of Ni salts and glycerol. This is because the oil-soluble ZCS QD cannot be well-dispersed in H_2O , and H_2O molecules cannot directly contact the ZCS QD surface. Fig. 7a shows the comparison of the photocatalytic H_2 -production rates of the ZCS RS, ZCS QD, ZCS QD with 1% cocatalyst and ZCS RS with 1% cocatalyst. The ZCS RS shows the lowest photocatalytic H_2 -production rate ($113 \mu\text{mol g}^{-1} \text{h}^{-1}$), which is caused by the rapid recombination of the photogenerated electron-hole pairs during the photocatalytic reaction. However, the ZCS QD shows an enhanced photocatalytic H_2 -production

Table 1

Fitted parameters obtained from the decay curves of the samples.

Samples	τ_1 (ns) (Rel. %)	τ_2 (ns) (Rel. %)	τ_3 (ns) (Rel. %)	τ_a (ns)
ZCS QD	0.26 (29.24%)	4.22 (24.03%)	16.61 (46.73%)	8.9
ZCS RS	0.24 (65.38%)	3.02 (21.88%)	13.46 (12.74%)	2.5

Fig. 7. (a) Photocatalytic H₂-production rates of ZCS RS, RS-1% Ni, QD, and QD-1% Ni. (b) Photocatalytic H₂ production over time for the ZCS QD and RS with 1% Ni.

activity (1220 μmol g⁻¹ h⁻¹), which is ~10.7 times higher than that of ZCS RS. The ZCS QD with 1% cocatalyst shows the highest photocatalytic H₂-production activity (2253 μmol g⁻¹ h⁻¹), which is higher than that of ZCS RS with 1% cocatalyst (313 μmol g⁻¹ h⁻¹). The photocatalytic H₂-production over time shows the significant difference between the two samples with 1% cocatalyst (Fig. 7b). The amounts of H₂ produced for two samples reach 16.3 and 3.9 mmol g⁻¹ after 9 h of irradiation, respectively. This result further demonstrates that the ZCS QD with 1% cocatalyst has a much higher photocatalytic H₂-production activity than the ZCS RS with 1% cocatalyst. We also compared the H₂-production rates of the current photocatalysts with those of previous Zn_xCd_{1-x}S-based ones. As shown in Table 2, ZCS QD-1% Ni, in this work, outperforms most of the photocatalysts reported previously. Thus, a small particle size, surface inorganic S ligand, and an introduced cocatalyst contribute to the enhanced photocatalytic H₂-production rate.

3.6. The reasons for enhanced photocatalytic H₂-production performance

The enhanced photocatalytic activities can be explained by following: First, the ZCS QD has a lower recombination rate of photogenerated electron-hole pairs than the ZCS RS because of the shorter transfer distance from the interior to the interface

of the ZCS QD [67]. Second, the surface inorganic S ligands of the ZCS QD (a) facilitate the sufficient dispersion of QD in water and increase the contact with water; (b) cause the ZCS QD to have close contact with the cocatalyst and reduce the distance between the ZCS QD with the cocatalyst, which is beneficial for electron transfer; (c) have a high hole capturing ability, i.e., the hole can quickly migrate from the interior to the S²⁻ surface to glycerol and be consumed quickly [54]. Thus, surface inorganic S ligands can also improve the charge-separation efficiency. Third, the ZCS QD has a small particle size and large specific surface area, which can expose additional active sites. Fourth, introducing a cocatalyst can further promote the separation of the photogenerated electron-hole pairs, reduce the H₂-production potential, and catalyze H₂ production.

The photocatalytic H₂-production mechanism of the samples is also discussed, as shown in Fig. 8a. During the photocatalytic H₂ production, electrons are excited from the VB to the CB and further migrate to Ni²⁺, thereby resulting in the partial reduction of Ni²⁺ ions to Ni⁰ atoms. Ni²⁺/Ni⁰ can act as a cocatalyst that can accelerate the transfer and separation of the photogenerated charge carriers, and the H⁺ can be reduced to H₂ molecules over Ni²⁺/Ni⁰. Meanwhile, the photogenerated holes can be consumed by glycerin. Fig. 8b shows the schematic illustration of the difference in the transfer distance of the carriers for the ZCS QD and RS. Photogenerated electrons and holes are transferred at a short transfer distance from the inner part

Table 2

Comparisons of the photocatalytic H₂-production performance of various Zn_xCd_{1-x}S-based photocatalysts.

Photocatalysts	Sacrifice agent	Light	Yield (μmol g ⁻¹ h ⁻¹)	Ref.
Zn _x Cd _{1-x} S-1% Ni	Glycerol	300 W Xe lamp	2253	This work
RGO/Zn _{0.5} Cd _{0.5} S	Na ₂ S-Na ₂ SO ₃	300 W Xe lamp	770	[59]
SiC/Zn _{0.5} Cd _{0.5} S	Na ₂ S-Na ₂ SO ₃	586 mW/cm ² Xe lamp	894	[60]
P-Zn _{0.5} Cd _{0.5} S	HMF	30 × 3 W LED	419	[61]
Cu ₂ S/Zn _{0.71} Cd _{0.29} S	Na ₂ S-Na ₂ SO ₃	100 mW/cm ² Xe lamp	1202	[62]
Ni ₃ C/Zn _{0.3} Cd _{0.7} S	Na ₂ S-Na ₂ SO ₃	300 W Xe lamp	3310.1	[63]
Hierarchical Zn _{0.64} Cd _{0.36} S	Na ₂ S-Na ₂ SO ₃	300 W Xe lamp	815	[64]
GO/Zn _{0.5} Cd _{0.5} S	Na ₂ S-Na ₂ SO ₃	150 W Xe lamp	1060	[65]
RGO/Zn _{0.8} Cd _{0.2} S	Na ₂ S-Na ₂ SO ₃	100 mW/cm ² Xe lamp	1824	[57]
CoPt ₃ /Zn _{0.5} Cd _{0.5} S	Na ₂ S-Na ₂ SO ₃	300 W	2830	[66]

Fig. 8. (a) Proposed mechanism of photocatalytic H₂ production. (b) The schematic illustration of the difference in transfer distance of carriers for ZCS QD and RS.

to the surface due to the small particle size of the ZCS QD, which reduces the possibility of recombination of photogenerated charge carriers. However, the ZCS RS has a relatively large particle size, thereby resulting in a long transfer distance from the inner part to the surface for photogenerated charge carriers. Thus, the ZCS QD shows significantly enhanced photocatalytic H₂-production performance. The formulas of the photocatalytic reaction process are as follows:

4. Conclusions

An oil-soluble ZCS QD photocatalyst is successfully synthesized by the hot-injection method. However, it exhibits very weak photocatalytic H₂-production activity due to its poor dispersion in water. Consequently, the oil-soluble ZCS QD is easily changed into a water-soluble ZCS QD by replacing the oil-soluble ligand with a water-soluble ligand. In the presence of a sacrificial agent, glycerin, the water-soluble ZCS QD exhibited good photocatalytic H₂-production rate (1220 μmol g⁻¹ h⁻¹), which was ~10.7 times higher than that of the ZCS RS (113 μmol g⁻¹ h⁻¹), due to its small particle size, large specific surface area, and good photogenerated carrier separation efficiency. The ZCS QD with 1% cocatalyst exhibited the highest photocatalytic H₂-production rate (2253 μmol g⁻¹ h⁻¹) and 15.9%

H₂-generation quantum efficiency at 420 nm light irradiation. This work provides new insights into the synthesis of QD photocatalysts.

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Graphical Abstract

Chin. J. Catal., 2021, 42: 15–24 doi: 10.1016/S1872-2067(20)63614-2

Zn_xCd_{1-x}S quantum dot with enhanced photocatalytic H₂-production performance

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The ZCS QD has a relatively small crystallite size, short photogenerated carriers transfer distance from the interior to the surface, and long carrier lifetime, resulting in a significantly enhanced photocatalytic H₂-production rate.

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锌镉硫量子点增强的光催化产氢活性

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摘要: 光催化分解水产氢是利用太阳能解决当今能源危机和环境污染问题的理想策略。硫化镉光催化剂由于具有较窄的

带隙、有效的光吸收能力、较负的导带位置和较强的还原能力等而受到广泛关注。然而,硫化镉光催化剂的光生电子-空穴复合速率高,导致其光催化活性比较低,因此在光催化领域的应用受到限制。为此,人们采取了很多方法来改善硫化镉光催化剂的光催化性能,例如加入助催化剂、构建异质结、表面修饰以及形成固溶体光催化剂等。

合成固溶体光催化剂被认为是提高硫化镉光催化活性最具有发展前景的方法之一,固溶体光催化剂通过形成轨道杂化而表现出可控的带隙和带边位置。在固溶体光催化剂中,锌镉硫胶体量子点引起了很多关注。锌镉硫胶体量子点的颗粒尺寸较小,这就使得光生电子和空穴由催化剂内部转移到表面的距离较短,增大了载流子分离效率。另外,锌镉硫胶体量子点具有较负的导带位置、可调控的带隙、较好的水中分散性以及良好的光吸收等优点,因此锌镉硫胶体量子点从其他光催化剂中脱颖而出。

本文分别采用热注法和传统共沉淀法制备了油溶性锌镉硫量子点和水溶性锌镉硫纳米颗粒。发现油溶性量子点亲水性能较差,几乎没有光催化活性,但油溶性量子点易通过配体交换过程转换成水溶性量子点,无机硫作为锌镉硫量子点的表面水溶性配体,可使量子点具有较好的亲水性。通过电化学测试、稳态荧光以及时间分辨荧光测试结果表明,相比于锌镉硫纳米颗粒,水溶性锌镉硫量子点具有更高的电子空穴分离效率。光催化产氢测试发现,在牺牲剂甘油存在的条件下,水溶性锌镉硫量子点的光催化产氢速率($1220 \mu\text{mol g}^{-1} \text{h}^{-1}$)显著提高,约是锌镉硫纳米颗粒产氢速率的10倍。加入助催化剂 Ni^{2+} 后,锌镉硫量子点表现出最高的光催化产氢活性($2253 \mu\text{mol g}^{-1} \text{h}^{-1}$),在420 nm灯的光照条件下,表观量子效率达到15.9%。光催化活性的增大主要归因于量子点较小的颗粒尺寸、表面无机硫配体以及助催化剂的添加,这些都有利于载流子的快速分离和转移,降低其复合,延长其寿命,并且加速了产氢动力学,因此提高了水溶性锌镉硫量子点的光催化产氢活性。

关键词: 锌镉硫化合物; 固溶体光催化剂; 光催化产氢; 油溶性量子点; 水溶性量子点

收稿日期: 2020-03-07. 接受日期: 2020-04-24. 出版日期: 2021-01-05.

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基金来源: 国家重点研发计划(2018YFB1502001); 国家自然科学基金(21871217, U1905215, 51961135303, 51932007, U1705251); 武汉理工大学材料复合新技术国家重点实验室创新基金(2017-ZD-4).

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