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Article

Enhanced photocatalytic H₂ production performance of CdS hollow spheres using C and Pt as bi-cocatalysts

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ABSTRACT

Photocatalytic H₂ production from water splitting is an effective method to solve energy crisis and environmental pollution simultaneously. Herein, carbon@CdS composite hollow spheres (C@CdS-HS) are fabricated via a facile hydrothermal method using porous carbon hollow spheres (C-HS) as the template. The C@CdS-HS shows an excellent photocatalytic H₂-generation rate of 20.9 mmol h⁻¹ g⁻¹ (apparent quantum efficiency of 15.3% at 420 nm), with 1.0 wt% Pt as a cocatalyst under simulated sunlight irradiation; this rate is 69.7, 13.9, and 3.9 times higher than that obtained with pure CdS hollow spheres (CdS-HS), C@CdS-HS, and CdS-HS/Pt, respectively. The enhanced photocatalytic H₂-evolution activity of C@CdS-HS/Pt is due to the synergistic effect of C and Pt as the bi-cocatalyst. The C-HS serves not only as an active site provider but also as an electron transporter and reservoir. Moreover, C-HS has a strong photothermal effect that is induced by near infrared light, which kinetically accelerates the H₂-production reaction. Additionally, the underlying charge transfer pathway and process from CdS to C-HS is revealed. This work highlights the potential application of C-HS-based nanocomposites in solar-to-chemical energy conversion.

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1. Introduction

The rapid consumption of fossil fuels and the severe pollution of the ecological environment are two major crises faced by humans [1]. Photocatalytic H₂ evolution from water splitting, which converts the inexhaustible solar energy to clean fuel (H₂), is considered one of the most promising methods to solve these issues [2–5]. Following Fujishima-Honda's precursor work in 1972, an explosive growth in the field of photocatalysts

has been reported in the last decades [6]. Among semiconductor photocatalysts, CdS has been extensively utilized as a promising candidate for hydrogen production due to its narrow band gap (E_g) (approximately 2.4 eV) for visible-light absorption and suitable band structure for water splitting [7–9]. However, single CdS shows poor photocatalytic H₂-production performance due to the fast recombination of photogenerated electron-hole pairs and serious photocorrosion [10]. To this end, multiple modification approaches, such as tuning the

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morphology and structure [11,12], constructing heterojunctions [13–20], and loading cocatalysts [21–27], have been adopted to ameliorate the photocatalytic performance of CdS. Loading cocatalysts is an outstanding strategy to enhance the light harvesting efficiency, promote charge separation, and create active sites in semiconductors [28–30].

Metallic cocatalysts with excellent performance have been widely reported in recent years, but their application is limited by their high cost and adverse impact on the environment [31–35]. Nonmetallic carbonaceous materials have been proven to be promising alternatives to metallic cocatalysts because of their low cost, environmental compatibility, excellent electronic conductivity, chemical stability, remarkable light absorption, and strong photothermal effect [36,37]. For instance, Bie et al. [38] deposited nitrogen-doped graphene onto CdS hollow spheres in situ and achieved remarkably enhanced photocatalytic CO₂ reduction performance. Fang et al. [39] reported that loading carbon dots on g-C₃N₄ leads to enhanced visible-light photocatalytic H₂ production. Meanwhile, carbon hollow spheres (C-HS) not only have the inherent advantages of carbonaceous materials but also possess a porous hollow structure, good structural stability, and extraordinary specific surface, making them potential cocatalysts [40]. Zhang et al. [41] prepared TiO₂/carbon hollow spheres and achieved superior visible-light photocatalytic efficiency for rhodamine B degradation. However, carbon loading onto the exterior surface of a photocatalyst leads to a shielding effect, which degrades the photocatalytic performance. Based on the abovementioned aspects, depositing CdS nanoparticles (NPs) onto the surface of C-HS seems to be a promising technique to enhance photocatalytic H₂-production performance.

Herein, C-HS was used as a template to deposit CdS NPs via a facile hydrothermal method and form a carbon@CdS composite hollow sphere (C@CdS-HS). Compared with pure CdS hollow spheres (CdS-HS), C@CdS-HS showed significantly enhanced photocatalytic hydrogen production activity, which originated from its large specific surface, increased light absorption from the ultraviolet (UV) to the near-infrared (NIR) region, efficient charge carrier separation, and strong photothermal effect. Furthermore, the charge transfer pathway and photocatalytic mechanism over the composite were elucidated by systematic characterizations.

2. Experimental

In accordance with a previous report [42], SiO₂@carbon spheres (SiO₂@C) were prepared using a method that involves the hydrolysis of tetraethyl orthosilicate (TEOS), polymerization of dopamine (DA), and a carbonization process. C-HS was prepared by etching the SiO₂ core of SiO₂@C with hot NaOH aqueous solution (1 M). C@CdS-HS was then fabricated via a facile hydrothermal method. For comparison, CdS-HS was also prepared using the same method except that SiO₂ was used as the template instead of SiO₂@C.

The details of the chemicals used, sample preparation, characterization, and photocatalytic H₂-production experiment are available in the Supporting Information.

3. Results and discussion

3.1. Synthesis and formation mechanism of C@CdS-HS

The overall C@CdS-HS photocatalyst synthesis is illustrated in Fig. 1 and is described as follows. A SiO₂@polydopamine sphere (SiO₂@PDA) was initially prepared via a one-step method involving the hydrolysis of TEOS and polymerization of dopamine at room temperature (RT). Then, the core-shell SiO₂@C was produced via the carbonization of SiO₂@PDA under a N₂ atmosphere and used as a template. The SiO₂@C was treated with an ultraviolet ozone cleaner for 0.5 h to introduce surface oxygen-containing groups for improved deposition of CdS NPs. Lastly, C@CdS-HS was fabricated via a facile hydrothermal method involving in situ heterogeneous nucleation and growth of CdS NPs, and dissolution of the SiO₂ core. The detailed reactions that occur during this method are described as follows [43]:

During hydrothermal synthesis, NH₃ released OH[−] to form an alkaline environment (Eq. (1)) and coordinated with cadmium ions (Cd²⁺) to form a tetra-ammine-cadmium (II) complex ([Cd(NH₃)₄]²⁺) (Eq. (2)). Then, the complex ions were adsorbed onto the surface of a negatively charged SiO₂@C, whose zeta potential was −30 mV (Fig. 2(a)). Afterward, sulfide ions (S^{2−}) and excess NH₃ were released from the continuous decomposition of thiourea in the hot alkaline environment (Eq. (3)). Subsequently, CdS NPs were deposited in situ onto the surface of the carbon shells when [Cd(NH₃)₄]²⁺ was combined with S^{2−} (Eq. (4)). Simultaneously, the SiO₂ core reacted with the abundant OH[−] produced by the excess NH₃ that was released from the decomposition of thiourea (Eq. (5)). As the reaction progressed, the SiO₂ core was fully etched and a hollow C@CdS-HS structure was eventually formed. This reaction process indicates that thiourea is a necessary additive that serves as a sulfur source and an etchant.

3.2. Structure and morphology

X-ray diffraction (XRD) analysis was performed to confirm the phase structure of CdS and investigate the crystallite size of the CdS NPs. As shown in Fig. 2(b), several typical peaks can be detected in the diffraction pattern of CdS-HS at 24.8°, 26.5°, 28.2°, 36.6°, 43.7°, 47.8°, and 51.8°, which correspond to the (100), (002), (101), (102), (110), (103), and (112) diffraction planes of the hexagonal CdS (JCPDS 41-1049), respectively [44].

Fig. 1. Schematic of C@CdS-HS synthesis.

Fig. 2. (a) Zeta potential of $\text{SiO}_2@\text{C}$ before and after treatment with an ultraviolet ozone cleaner; (b) XRD patterns of C-HS, CdS-HS, and C@CdS-HS.

The spectrum of C-HS has a broad peak positioned at $\approx 22^\circ$, which can be assigned to the (002) plane of amorphous carbon. In the case of C@CdS-HS, the diffraction pattern can be considered an overlap of those for CdS-HS and C-HS, indicating successful integration of the two components and the identical phase structure of CdS in CdS-HS and C@CdS-HS. Furthermore, the broad diffraction peaks in CdS-HS and C@CdS-HS imply a small crystallite size of the CdS NPs, which shortens the transfer path of the photogenerated charges from the interior to the surface of the CdS NPs [45]. The solubility product constant (K_{sp}) of CdS (1.40×10^{-29}) is small [46], and hence, the growth of CdS crystals is rapid. Fortunately, during the hydrothermal process in this study, NH_3 acts as a Cd^{2+} capping agent (Eq. (2)) and retards the growth of CdS crystals (Eq. (4)), thus resulting in a decrease in the crystallite size of CdS.

The morphologies of the samples were observed via field-emission scanning electron microscopy (FESEM). As shown in Figs. 3(a) and (b), the prepared $\text{SiO}_2@\text{PDA}$ and C-HS are uniformly sized and regularly shaped nanospheres with a diameter of ~ 300 and 200 nm, respectively. Figs. 3(c) and (d) show that C@CdS-HS and CdS-HS have similar morphologies with a narrow size distribution (average diameter of ~ 250 nm).

Fig. 3. FESEM images of $\text{SiO}_2@\text{PDA}$ (a), C-HS (b), C@CdS-HS (c), and CdS-HS (d). The inset of (c) and (d) shows corresponding high-magnification images.

In addition, the high-magnification FESEM images (inset of Figs. 3(c) and (d)) show that the exterior shells are composed of numerous CdS NPs with diameters of approximately 10 nm and are well-ordered. The microstructures of C@CdS-HS and CdS-HS were further characterized via transmission electron microscopy (TEM), and both showed a hollow spherical morphology (Figs. 4(a) and (c)). Interestingly, C@CdS-HS had a rougher cavity edge compared with CdS-HS. This rough edge could be ascribed to the deposition and stuffing of CdS NPs in mesopores on the C-HS surface, indicating that an intimate contact interface is formed between the CdS NPs and C-HS. As shown in the high-resolution TEM (HRTEM) images (Figs. 4(b)

Fig. 4. (a,b) TEM and HRTEM images of C@CdS-HS. (c,d) TEM and HRTEM images of CdS-HS. (e) EDX mapping images of C@CdS-HS. The inset in (b) and (d) shows the corresponding SAED patterns.

Fig. 5. (a) Raman spectra (inset is the enlarged spectra) and (b) nitrogen adsorption-desorption isotherms (inset shows the pore size distribution) of C-HS, CdS-HS, and C@CdS-HS.

and (d)), the thickness of the CdS shell in C@CdS-HS and CdS-HS is 20–30 nm. The lattice fringes with a length of 0.36 and 0.32 nm correspond to the (100) and (101) lattice planes of the hexagonal CdS, respectively. This result is consistent with the corresponding selected-area electron diffraction (SAED) and XRD patterns. To determine the composition and element distribution of the composite, EDX mapping was conducted. As shown in Fig. 4(e), Cd and S elements are evenly distributed in the exterior shell, whereas the C element is mainly distributed in the interior shell, further confirming that C@CdS-HS is composed of C and CdS. The C element in the lower right corner is derived from the carbon film on the copper mesh.

As shown in Fig. 5(a), two Raman scattering peaks positioned at 298 and 597 cm⁻¹ can be observed for CdS-HS, which represent the first- and second-order longitudinal optical modes of CdS, respectively [47]. The C-HS sample shows the D and G bands of graphitic carbon at 1350 and 1605 cm⁻¹, respectively [48,49]. In the spectrum of C@CdS-HS, all the above peaks are observed, thus confirming the integration of CdS and C-HS in the composite. In addition, the D band is related to the defective and disordered carbon, while the G band arises from the *sp*² bonding carbon. The appearance of the G band confirms the presence of graphitic carbon in C-HS, which is the reason for the excellent electronic conductivity of C-HS. Furthermore, the defect level of carbonaceous materials can be determined from the intensity ratio of the D band to the G band (*I*_D/*I*_G). C@CdS-HS exhibits a higher *I*_D/*I*_G (0.84) ratio than that of C-HS (0.74), indicating that the hydrothermal treatment increased the concentration of defects.

To determine the porous structure and specific surface area of the samples, adsorption-desorption isotherms were measured. As shown in Fig. 5(b), according to the Brunauer-Emmett-Teller classification, all the samples show type-IV isotherms, indicating the existence of mesopores [50,51]. The C-HS and CdS-HS samples exhibit typical H3 hysteresis loops, implying the existence of slit-like pores formed by the accumulation of nanospheres [52]. In the case of C@CdS-HS, the hysteresis loop is a combination of H2- and H3-type hysteresis loops, suggesting the existence of ink-bottle

pores formed by the deposition and accumulation of CdS NPs on the surface of C-HS. Additionally, the pore size distribution curves reveal that C-HS has more micropores than does CdS-HS. Therefore, the introduction of C-HS can increase the number of micropores in the composite, thereby increasing its specific surface area. The Brunauer-Emmett-Teller (BET) specific surface area (*S*_{BET}) and pore parameters of the samples are presented in Table 1. The *S*_{BET} value of C@CdS-HS (166 m² g⁻¹) shows a more significant improvement compared with that of CdS-HS (37 m² g⁻¹). This is due to the large *S*_{BET} of C-HS (252 m² g⁻¹), which can provide additional active sites for photocatalytic reactions.

3.3. Photocatalytic hydrogen evolution performance

The photocatalytic H₂-generation activities of samples were evaluated under simulated sunlight irradiation in 10 vol% lactic acid aqueous solution. As shown in Fig. 6(a), no hydrogen evolution activity was observed for C-HS. The C@CdS-HS exhibits a H₂-generation rate of 1.5 mmol g⁻¹ h⁻¹, which is five times higher than that of CdS-HS (0.3 mmol g⁻¹ h⁻¹). The carbon content of C@CdS-HS was 21.1 wt%, as measured by CHNS/O element analyzer, indicating that the actual activity of CdS in C@CdS-HS is much higher than that in CdS-HS. Pt is the best among H₂-production cocatalysts; thus, the H₂-production performance of CdS-HS is greatly enhanced in the presence of 1.0 wt% Pt, and its rate is 17.7 times higher than that of CdS-HS without a cocatalyst. Surprisingly, when 1.0 wt% Pt is deposited onto the surface of C@CdS-HS, the C@CdS-HS/Pt sample achieves its greatest H₂-generation rate (20.9 mmol h⁻¹ g⁻¹), which is 69.7 times higher than that of pure CdS-HS (0.3 mmol g⁻¹ h⁻¹). The apparent quantum efficiency of C@CdS-HS/Pt is

Table 1
*S*_{BET} and pore parameters of C-HS, CdS-HS, and C@CdS-HS.

Samples	<i>S</i> _{BET} (m ² g ⁻¹)	Average pore diameter (nm)	Total pore volume (cm ³ g ⁻¹)
C-HS	252	5.8	0.37
CdS-HS	37	9.9	0.09
C@CdS-HS	166	5.6	0.23

Fig. 6. (a) Photocatalytic H_2 -generation rates of the samples with 10 vol% lactic acid aqueous solution as a sacrificial reagent under simulated sunlight irradiation; (b) Cyclic photocatalytic H_2 -generation curves of C@CdS-HS/Pt.

15.3% at a wavelength of 420 nm. The above results show that C and Pt can synergistically improve the photocatalytic H_2 -generation performance of CdS. In the cyclic photocatalytic H_2 -generation experiment (Fig. 6(b)), the C@CdS-HS/Pt shows good recyclability of over four runs totaling 12 h.

3.4. Light absorption and photothermal effect

Given that light is the driving force for the generation of charge carriers, the light absorption ability and range of the photocatalyst are important. The light absorption ability and range of the samples were evaluated by ultraviolet-visible-near infrared (UV-Vis-NIR) diffuse reflectance spectra (DRS). As shown in Fig. 7(a), CdS-HS shows absorption only in a narrow UV-Vis region (200–540 nm), which is just a small fraction of the solar energy. The E_g of CdS-HS is 2.31 eV, as calculated from

the Kubelka-Munk function [53] (Fig. 7(b)). After being composited with C-HS, C@CdS-HS exhibits a remarkably enhanced absorption in the UV-Vis-NIR region (200–2500 nm) and this improvement is ascribed to the full-spectrum absorption of C-HS. This result is consistent with its black color, as shown in Fig. 7(a). The interior C-HS has no light shielding effect on CdS. In addition, NIR light absorption can accelerate molecular vibration that generates additional heat, leading to a strong photothermal effect [54]. To investigate the photothermal effect caused by C-HS, infrared thermograms of the samples were obtained after illumination (3 W, 760 nm) for 1 min at RT (Figs. 7(c)–(e)). The maximum temperature of CdS-HS increased by only 1.9 °C from RT, whereas the maximum temperature of C@CdS-HS and C-HS increased by 6.8 and 7.5 °C, respectively, after 1 min of illumination. This result confirms the strong photothermal effect of C-HS on the composite. The heat gener-

Fig. 7. (a) UV-Vis-NIR DRS of C-HS, CdS-HS, and C@CdS-HS. (b) Band gap obtained from the Kubelka-Munk function of CdS-HS. (c–e) Infrared thermograms of CdS-HS, C@CdS-HS, and C-HS after illumination by a 760 nm LED for 1 min at RT.

ated by C-HS can increase the surface temperature of CdS and accelerate the desorption of H_2 from reaction sites, thus kinetically facilitating the photocatalytic H_2 production reaction. The above results indicate that the composite can efficiently utilize solar energy.

3.5. Separation and transfer of photogenerated charge carriers

In addition to the light absorption capacity, the separation and transfer of photogenerated charge carriers are important factors in determining photocatalytic activity. The photoluminescence (PL) spectra were obtained to explore the separation efficiency of photogenerated charge carriers. As shown in Fig. 8(a), two peaks of the C@CdS-HS located at 540 and 633 nm exhibit a significantly decreased PL intensity in comparison with CdS-HS. These peaks correspond to the intrinsic radiative recombination of photogenerated charge carriers and impurity level emission, respectively. This result demonstrates the low recombination possibility and high separation efficiency of photogenerated electron-hole pairs in C@CdS-HS.

Time-resolved photoluminescence (TRPL) was used to characterize the transfer behavior of the photogenerated charge carriers. The average fluorescence lifetime (τ_a) is mainly determined by the radiative transition lifetime (τ_1) and nonradiative transition lifetime (τ_2). An extra nonradiative transition leads to a decrease in τ_2 . As presented in Fig. 8(b), τ_2 of C@CdS-HS decreases from 3.86 to 3.45 ns in comparison with CdS-HS, whereas τ_1 does not significantly change (0.30 ns for CdS-HS and 0.29 ns for C@CdS-HS). As a result, τ_a of C@CdS-HS decreases from 2.08 to 1.66 ns. This result illustrates that C@CdS-HS has extra nonradiative pathways provided by C-HS for photogenerated electron transfer, which accounts for the decreased τ_a and reduced photoluminescence intensity [55].

Therefore, the photogenerated electrons on the conduction band (CB) of CdS transfer to C-HS and are temporarily stored in the C-HS, resulting in the low recombination rate and high separation efficiency of photogenerated charge carriers.

To further confirm the enhanced separation and transfer efficiency of photogenerated charge carriers over C@CdS-HS, the transient photocurrent response (TPR) was measured by several on-off cycles of a 420 nm light-emitting diode (LED) intermittent irradiation. Fig. 8(c) shows that C@CdS-HS exhibits much higher photocurrent density compared with CdS-HS, suggesting that the photogenerated charge carriers of C@CdS-HS have a more efficient separation and transfer compared with those of CdS-HS. In addition, the photocurrent decay of C@CdS-HS is slower than that of CdS-HS, implying that the photogenerated electrons, that were separated and stored in the C-HS, transfer to CdS again. The above results further confirm the ability of C-HS to separate and store photogenerated electrons. With 1.0 wt% Pt deposition, C@CdS-HS/Pt and CdS-HS/Pt show higher photocurrent density, indicating that Pt NPs can further promote the separation of photogenerated charge carriers and dramatically enhance H_2 production of C@CdS-HS [56].

The interfacial charge transfer rate was explored via electrochemical impedance spectroscopy, and the Nyquist plots of the samples are displayed in Fig. 8(d). The semicircular diameter of the Nyquist plots indicates the interfacial electron transfer resistance of the samples [57]. The C-HS exhibits minimum resistance due to its excellent electronic conductivity, whereas the CdS-HS exhibits maximum resistance. As expected, the C@CdS-HS shows a decreased resistance in comparison with CdS-HS due to the introduction of C-HS, indicating that the composite has an improved interfacial charge transfer rate. Additionally, the resistance of CdS-HS/Pt and C@CdS-HS/Pt

Fig. 8. PL spectra (a) and TRPL decay curves (b) of CdS-HS and C@CdS-HS; TPR (c) and Nyquist plots (d) of C-HS, CdS-HS, CdS-HS/Pt, C@CdS-HS, and C@CdS-HS/Pt.

Fig. 9. (a) Contact potential differences (CPDs) of the samples; (b) Mott-Schottky plots of CdS-HS at frequencies of 3000, 2000, and 1000 Hz.

decreased to a certain extent in comparison with that of CdS-HS and C@CdS-HS, respectively, due to the good electronic conductivity of Pt. In summary, the C-HS can serve as an electron reservoir and transporter, that can boost the separation and transfer efficiency of photogenerated charge carriers and dramatically enhance the photocatalytic H_2 -production activity of CdS.

3.6. Charge transfer pathway and photocatalytic mechanism

To clarify the pathway and process of photogenerated charge transfer, the energy band structure of the photocatalyst must be determined. A Kelvin probe was used to determine the work function (W) and Fermi level (E_f) of the samples. As shown in Fig. 9(a), the CPDs of the samples were measured in the dark and under 427 nm light illumination conditions. The W and E_f of the samples were calculated in accordance with the following equations [58]:

$$W_{\text{sample}} = W_{\text{probe}} + e \times \text{CPD}_{\text{sample}}, \quad (6)$$

$$E_f = E_{\text{vac}} - W_{\text{sample}}, \quad (7)$$

where W_{sample} is the W value of the sample, W_{probe} is the W value of the gold probe (≈ 4.25 eV), e is the charge of the electron, $\text{CPD}_{\text{sample}}$ is the CPD value of the sample, and E_{vac} is the energy of a static electron at vacuum level (0 eV). The obtained CPD, W , and E_f of the samples are summarized in Table 2. Before illumination, Pt had the largest W_{dark} (4.877 eV) and the lowest $E_{f(\text{dark})}$ (-4.877 eV), followed by C-HS and CdS-HS. After the combination of these three constituents, C@CdS-HS/Pt shows an intermediate $E_{f(\text{dark})}$ (-4.613 eV), that is between that of C-HS (-4.656 eV) and CdS-HS (-4.445 eV). This result is attributed to the electron transfer from CdS to Pt and C.

Additionally, the Mott-Schottky plots of CdS-HS were created via electrochemical techniques at three frequencies to de-

termine the flat band potential (E_{fb}) of CdS. As shown in Fig. 9(b), the positive slopes of the Mott-Schottky plots confirm the n-type feature of CdS, and the E_{fb} of CdS was determined to be -0.66 V vs. the normal hydrogen electrode (NHE). The CB potential (E_{CB}) of CdS was calculated to be -0.76 V (vs. NHE) because E_{CB} is more negative at approximately -0.1 V compared with the E_{fb} of an n-type semiconductor [59]. In accordance with the value of E_g in Fig. 7(b), the valence band potential (E_{VB}) of CdS was calculated to be 1.55 V (vs. NHE) using the following equation [60,61]:

$$E_{VB} = E_{CB} + E_g \quad (8)$$

Based on the above results, the band structure of the samples and charge carrier transfer pathway are illustrated in Fig. 10. Before illumination and contact, the E_f of CdS was higher than that of Pt and C-HS. After contact, the free electrons transferred from CdS to Pt and C to achieve Fermi level equilibrium, resulting in an upward band bending and the Schottky barrier. After illumination on the C@CdS-HS/Pt system, electrons were excited from CdS VB to CB, leading to a higher E_f of CdS compared with that of Pt and C-HS. To establish a new equilibrium state of E_f , photogenerated electrons were further injected into Pt and C over the Schottky barrier to participate in the H_2 generation reaction, whereas the holes that remained in CdS were consumed by the sacrificial agent. Consequently, the photogenerated electron-hole pairs were spatially separated, thus effectively enhancing the photocatalytic H_2 production of C@CdS-HS.

The pathway of the photogenerated charge transfer was further confirmed via in situ irradiated X-ray photoelectron

Table 2

CPD, W , and E_f of the samples before and after illumination.

Samples	CPD _{dark} (mV)	CPD _{light} (mV)	W_{dark} (eV)	W_{light} (eV)	$E_{f(\text{dark})}$ (eV)	$E_{f(\text{light})}$ (eV)
CdS-HS	195	62	4.445	4.312	-4.445	-4.312
C@CdS-HS	329	205	4.579	4.455	-4.579	-4.455
C@CdS-HS/Pt	363	249	4.613	4.499	-4.613	-4.499
C-HS	406	406	4.656	4.656	-4.656	-4.656
Pt	627	627	4.877	4.877	-4.877	-4.877

Fig. 10. Energy band structure and the photogenerated charge transfer pathway.

Fig. 11. High-resolution XPS spectra of Cd 3d (a), S 2p (b), and Pt 4f (c) of the samples in the dark and under UV irradiation (C@CdS-HS/Pt UV).

spectroscopy (XPS). As shown in Fig. 11, the Cd 3d XPS spectra exhibit two peaks corresponding to Cd $3d_{5/2}$ and Cd $3d_{3/2}$, while the S 2p XPS spectra reveal two peaks assigned to S $2p_{3/2}$ and S $2p_{1/2}$. In addition, two peaks designated to Pt $4f_{7/2}$ and Pt $4f_{5/2}$ can be found in the Pt 4f XPS spectra. The peaks of Cd 3d and S 2p in C@CdS-HS shifted positively (0.2 and 0.3 eV, respectively) in comparison with those of CdS-HS, demonstrating the transfer of free electrons from CdS to C after combination. This result confirms the ability of C to separate and accept electrons. After 1.0 wt% Pt deposition on C@CdS-HS, the peaks further shifted positively, indicating that part of the free electrons transferred from CdS to Pt. Furthermore, after UV irradiation, the binding energies of Cd 3d and S 2p in C@CdS-HS/Pt became more positive, whereas the peaks of Pt 4f in C@CdS-HS/Pt shifted negatively. This result implies that the photogenerated electrons transferred from CdS to Pt. The peaks of Pt 4f in C@CdS-HS/Pt shifted positively by 0.2 eV in comparison with CdS-HS/Pt, indicating that the acceptance of electrons by C and Pt was a competitive process, and electrons were transferred from CdS to C and Pt simultaneously. The above experimental results are highly consistent with the charge transfer pathway in Fig. 10.

Lastly, the photocatalytic mechanism over C@CdS-HS/Pt was proposed based on the above discussions and is illustrated in Fig. 12. Under sunlight irradiation, CdS is excited to produce photogenerated electrons and holes. The photogenerated electrons in CdS subsequently transfer to C and Pt simultaneously and then reduce water to generate H_2 , whereas the holes left in CdS are consumed by lactic acid. C acts as an electron reservoir,

which boosts the separation and transfer of photogenerated charge carriers. Meanwhile, C has a strong photothermal effect that is induced by its intense absorption of NIR light. This kinetically facilitates the photocatalytic H_2 production reaction by increasing the local temperature.

4. Conclusions

C-HS with a porous hollow structure, large specific surface, good electronic conductivity, and excellent NIR light absorption was used as a template to deposit CdS NPs via a facile hydrothermal method and thus fabricate C@CdS-HS for photocatalytic H_2 generation. The C@CdS-HS exhibits an excellent photocatalytic H_2 -evolution rate of 20.9 mmol $h^{-1} g^{-1}$, with 1.0 wt% Pt as a cocatalyst under simulated sunlight irradiation. This rate is 69.7, 13.9, and 3.9 times higher than that of CdS-HS, C@CdS-HS, and CdS-HS/Pt, respectively. Based on the systematic characterization results, a photogenerated charge transfer pathway is elucidated, and a photocatalytic mechanism for C@CdS-HS/Pt composites is proposed. It was shown that C-HS with a porous hollow structure and large specific surface can provide additional active sites for H_2 production reaction. Furthermore, C-HS serves as an electron reservoir and transporter and promotes the separation and transfer of photogenerated charge carriers. Moreover, the strong photothermal effect of C-HS that is induced by its intense absorption of NIR light can efficiently utilize solar energy. In the presence of Pt, the photocatalytic H_2 -production activity of C@CdS-HS significantly increases, indicating the cooperative effect of C and Pt as bi-cocatalysts. In summary, the significant enhancement of photocatalytic activity is mainly attributed to enhanced light absorption, strong photothermal effect, improved charge transfer and separation, and bi-cocatalyst synergistic effect. This study is potentially applicable to a series of C-HS supported photocatalysts to ameliorate their photocatalytic performance and heuristic for comprehensive utilization of solar energy.

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Fig. 12. Photocatalytic H_2 -generation mechanism over C@CdS-HS/Pt.

Graphical Abstract

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Enhanced photocatalytic H₂ production performance of CdS hollow spheres using C and Pt as bi-cocatalysts

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Carbon@CdS composite hollow spheres (C@CdS-HS) are fabricated using carbon hollow spheres (C-HS) as a template, and they show excellent photocatalytic H₂-production activity with C and Pt as bi-cocatalysts.

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碳铂双助催化剂增强CdS空心球光催化产氢性能

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摘要: 利用半导体光催化分解水产氢是将太阳能转换为化学能最有前景的方法之一。在众多的半导体光催化剂中, 硫化镉(CdS)不仅具有可见光响应的带隙值(约2.4 eV), 而且其导带底和价带顶的能级横跨于水的氧化还原电势两端, 能够在可见光照射下分解水产氢, 这使得CdS成为一种热门的光催化剂而被广泛研究。然而, 单一CdS由于光生电子-空穴对复合速率快、光腐蚀严重等缺点, 其光催化产氢活性并不高。为了克服这些缺点, 人们探索了多种改性策略, 如形貌和结构调控、构建异质结以及负载助催化剂等。

负载助催化剂由于可以增强光吸收、促进光生电荷分离以及提供更多活性位点, 被认为是一种有效的改性策略。然而, 目前大部分的助催化剂都是金属材料, 不仅价格昂贵, 而且容易对环境造成污染破坏。碳材料因为具有经济环保、导电性能优异、化学稳定性好、光吸收能力和光热效应强等优点, 成为一种有望实现太阳能高效综合利用的非金属助催化剂。其中, 空心碳球还具有质量轻、比表面积大以及光利用率高独特优势, 吸引了广大科研工作者的注意。

本文选取多孔碳空心纳米球(C-HS)作为模板, 通过简单的水热法制备了carbon@CdS空心球(C@CdS-HS)复合光催化剂, 并将其用于光催化分解水产氢。作为对照, 在相同的条件下制备了单一的CdS空心球(CdS-HS)。在模拟太阳光照射下并沉积1.0 wt% Pt后, C@CdS-HS/Pt的光催化产氢速率高达20.9 mmol h⁻¹ g⁻¹ (420 nm处的表观量子效率为15.3%), 分别是CdS-HS、C@CdS-HS和CdS-HS/Pt的69.7、13.9和3.9倍。通过一系列表征手段, 揭示了光生电荷的传输路径, 并提出了C@CdS-HS/Pt光催化活性增强的机理, 多孔C-HS的引入提高了复合光催化剂的比表面积, 增加了反应活性位点; 导电性良好的C-HS可以起到贮存和传导光生电子的作用, 从而提高光生载流子的分离和传输效率; CdS纳米颗粒原位生长在C-HS表面形成紧密接触的界面, 有利于光生电荷在界面间的传输; C-HS吸收红外光产生很强的光热效应, 可以使复合光催化剂的表面温度显著升高, 在动力学上提高催化剂的产氢速率; C-HS和Pt作为双助催化剂具有明显的协同效应, 可以显著提高CdS的光催化产氢活性。

关键词: CdS空心球; 碳; 铂; 双助催化剂; 协同效应; 光催化产氢

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