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Improved visible-light photocatalytic H₂ generation over CdS nanosheets decorated by NiS₂ and metallic carbon black as dual earth-abundant cocatalysts

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ABSTRACT

CdS nanosheets (NSs) photocatalysts modified with dual earth-abundant co-catalysts of metallic carbon black (CB) and NiS₂ were synthesized by a two-step solvothermal/impregnation method. All the experiment results demonstrated that the co-loading of CB and NiS₂ could significantly enhance the photocatalytic H₂-evolution activity of CdS NSs. The photocatalytic performance of the as-prepared CdS/CB/NiS₂ samples was tested under visible light ($\lambda \geq 420$ nm) by using an aqueous solution containing 0.25 mol L⁻¹ Na₂S-Na₂SO₃ as the sacrifice agent. The CdS-0.5%CB-1.0%NiS₂ composite photocatalysts exhibited the highest H₂-evolution rate of 166.7 $\mu\text{mol h}^{-1}$, which was approximately 5.16 and 1.87 times higher than those of pure CdS NSs and CdS-1.0%NiS₂, respectively. The possible mechanism for the enhanced H₂-evolution activity of CdS/CB/NiS₂ composite photocatalysts was proposed. The results showed that the enhanced photocatalytic H₂-evolution activities could be ascribed to the co-loading of metallic CB and NiS₂ as co-catalysts onto the surface of CdS NSs. The excellent synergetic effect between the CB and NiS₂ could obviously improve visible light absorption, promote separation of photogenerated electron-hole pairs and boost the H₂-evolution kinetics, thus leading to an enhanced activity for H₂ evolution. More interestingly, the metallic CB could not only act as a cocatalyst for H₂ evolution, but also serve as a conductive electron bridge to promote the charge migration. This work not only demonstrates that loading CB as a co-catalyst is a promising strategy to further boost the photocatalytic activity of CdS/NiS₂ composites, but also offers a new mechanistic insight into the construction of highly efficient and stable CdS NSs-based hybrid photocatalysts with dual earth-abundant co-catalysts for photocatalytic applications.

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1. Introduction

Hydrogen (H₂) is a promising and clean alternative energy for the fossil fuels [1,2]. Since Fujishima et al. [3] first achieved

overall water splitting in a TiO₂-Pt photoelectrochemical cell under ultraviolet (UV) light in 1972, various inorganic and organic semiconductors, including metal oxides [4–8], sulfides [9–11], nitrides [12], metal-organic frameworks (MOFs) [13],

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and metal-free graphitic carbon nitride (g-C₃N₄) [14–18], have been exploited for H₂ evolution under solar light. Among them, cadmium sulfide (CdS) is considered an attractive semiconductor for visible light H₂ evolution because of its narrow band gap (2.4 eV) and suitable conduction band position [9,19,20]. However, several persistent issues still hinder the large-scale application of CdS photocatalysts, including rapid charge-carrier recombination and strong photocorrosion, which lead to low photocatalytic activity and durability. To overcome these problems, many modifications have been investigated to improve the photocatalytic H₂-evolution activity of CdS photocatalysts [21], such as fabricating micro/nanoporous structures [15,22–25], constructing heterojunctions [26–29] and Z-scheme systems [30–32], designing solid solutions [33], coupling with nanocarbons [20,34–37], and loading cocatalysts [38,39]. In particular, the fabrication of nanostructured CdS and loading of appropriate cocatalysts are considered the most promising modification strategies for boosting the photocatalytic activity of CdS photocatalysts.

Recently, various nanostructured CdS photocatalysts, such as quantum dots/nanoparticles [40], nanorods/nanowires [41,42], and hierarchical nanoflowers [22,43], have been widely exploited to achieve enhanced photocatalytic H₂ evolution or CO₂ reduction by shortening the migration distance of carriers and reducing defects in CdS crystals. However, interesting ultrathin 2D CdS nanosheet photocatalysts have seldom been reported for photocatalytic H₂ evolution owing to their complicated fabrication process. In 2013, Xu et al. [44] synthesized ultrathin 2D CdS nanosheets of 4-nm thickness for photocatalytic H₂ evolution via a simple solvothermal and solution-phase ultrasonic exfoliation approach using CdS-DETA hybrid nanosheets as starting materials. In another study, ultrathin CdS nanosheets were synthesized via a facile solvothermal method using cadmium acetate and sulfocarbamide as raw materials [45]. These reports provide new strategies for the construction of 2D CdS nanosheet-based composite photocatalysts for various photocatalytic reactions. In this regard, the further investigation of photocatalytic H₂ generation over CdS nanosheets is an interesting and attractive prospect.

Expensive noble metals, such as Pt [46] and plasmonic Au [47,48], are usually deposited on the surface of nanostructured CdS as cocatalysts to effectively reduce the recombination of photogenerated electron–hole pairs, which significantly boosts the photocatalytic H₂ evolution [46]. However, because of the high cost and limited reserves of these noble metals, the design and development of highly efficient and earth-abundant noble-metal-free cocatalysts to boost photocatalytic H₂ evolution over nanostructured CdS remains important. Various earth-abundant cocatalysts have been widely exploited to enhance photocatalytic H₂ evolution over CdS, including MoS₂ [49], WS₂ [50,51], NiS [42,52], WC [53], CuS [54], amorphous Ni(OH) [55], and Co₃O₄ [41,56]. Notably, NiS₂ has been found to act as an efficient noble-metal-free cocatalyst to improve the photocatalytic H₂ evolution yield of CdLa₂S₄ [57] and C₃N₄ [58,59], perhaps due to its interesting electrical and optical properties [60]. To our knowledge, there have been no reports of CdS decorated by NiS₂ cocatalyst for promoting photocatalytic H₂

Scheme 1. Fabrication of CdS/CB/NiS₂ photocatalysts.

evolution. Furthermore, the weak electrical conductivity and low work function of earth-abundant cocatalysts still significantly limits the enhancement in photocatalytic H₂ evolution yield, which might be due to the unfavorable collection and utilization of photogenerated electrons caused by loose interface contacts. Interestingly, coupling metallic nanocarbon materials (such as carbon black, acetylene black, and graphene) with earth-abundant cocatalysts has been demonstrated as an efficient strategy to remedy these disadvantages, owing to their strong electrical conductivity, enhanced visible-light absorption, effective charge separation, and increased active sites [61–63]. Accordingly, loading cheap metal-free carbon black and NiS₂ as dual cocatalysts could potentially boost the photocatalytic H₂-evolution activity of CdS nanosheets (NSs), but has yet to be reported.

In this study, NiS₂ and carbon black were used for the first time as dual earth-abundant cocatalysts to improve the photocatalytic H₂ evolution activity of CdS NSs. The ternary CdS/CB/NiS₂ composite photocatalysts were successfully synthesized using a facile two-step solvothermal/impregnation method (Scheme 1). The photocatalytic H₂-evolution activity of the composite photocatalysts was tested using a Na₂S–Na₂SO₃ aqueous solution (0.25 mol L^{−1}) as a sacrifice agent under visible light ($\lambda \geq 420$ nm). All results indicated that the ternary CdS/CB/NiS₂ composite exhibited much better photocatalytic H₂-evolution activity than pure CdS NSs and the binary CdS/NiS₂ composite. Carbon black can act not only as a cocatalyst to boost H₂ evolution, but also as an electron transfer bridge between the CdS NSs and NiS₂. A possible mechanism for the enhancement in photocatalytic H₂-evolution activity of the ternary CdS/CB/NiS₂ composite was also proposed.

2. Experimental

2.1. Preparation of photocatalysts

2.1.1. Materials

All materials were of analytical grade and used as received, including cadmium acetate (Cd(Ac)₂·2H₂O), sulfocarbamide, ethylenediamine (EDA), nickel nitrate (Ni(NO₃)₂), sodium hydroxide (NaOH), and thiacetamide (TAA).

2.1.2. Synthesis of CdS NSs

CdS NSs were synthesized using a facile solvothermal method [45]. Cd(Ac)₂·2H₂O (2.0 mmol) and SC(NH₂)₂ (6.0 mmol) were added to EDA (60 mL) with vigorous stirring. After

30 min, the suspension was transferred to a 100-mL Teflon-lined autoclave and heated at 100 °C for 8 h. After allowing to cool to room temperature, the bright yellow precipitate was centrifuged at 8000 r/min for 5 min and then washed three times with ethanol and deionized water to remove organic solvent, respectively. Finally, the product was dried at 60 °C for 8 h in a vacuum drying oven.

2.1.3. Synthesis of binary CdS/NiS₂

Binary CdS/NiS₂ was prepared using a simple impregnation method [59]. In brief, Ni(NO₃)₂ was used as the NiS₂ precursor. The CdS NSs (600 mg) were dispersed in deionized water (60 mL) by ultrasonication and stirring. Next, Ni(NO₃)₂ aqueous solution (0.1 mol L⁻¹, 1.2 mL) was added to the dispersion and stirred for 30 min at room temperature. The Ni²⁺ ions became bound to the surface of CdS NSs through chemical adsorption under constant vigorous stirring. Next, TAA solution (1 mol L⁻¹, 2.4 mL) was added to the above mixed solution. After constant stirring at room temperature for 10 min, the mixed solution was heated at 80 °C for 12 h. Finally, the products were centrifuged (8000 rpm), washed with distilled water three times, and dried at 60 °C for 10 h in a vacuum drying oven. The as-prepared CdS/NiS₂ composite photocatalyst containing 1 wt% NiS₂ was denoted as CdS–1%NiS₂.

2.1.4. Synthesis of CdS/CB/NiS₂ composites

Binary CdS/CB composites were synthesized by mixing a certain mass ratio of CdS and CB via ultrasonication. The appropriate mass ratio of CdS and CB powder was added to a beaker containing absolute ethanol (60 mL) and sonicated for 2 h. The final product was centrifuged (7000 r/min), washed with ethanol and deionized water, and then dried in an oven at 60 °C for 8 h. The as-prepared CdS/CB composites were used to prepare CdS/CB/NiS₂ samples via a procedure similar to that described above for CdS/NiS₂. The resultant CdS/CB/NiS₂ samples containing 0.5, 1, 1.5, and 2 wt% CB were denoted as CdS–0.5%CB–1%NiS₂, CdS–1%CB–1%NiS₂, CdS–1.5%CB–1%NiS₂, and CdS–2%CB–1%NiS₂, respectively.

2.2. Characterization

The crystal structure of CdS/CB/NiS₂ was analyzed by X-ray diffraction (XRD; MSAL-XD2 diffractometer with Cu K_α radiation) at a scan rate of 8° min⁻¹. The morphology was determined by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) (JEM-2100HR 200 kV, Japan) at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed with a VG ESCALAB250 surface analysis system using a monochromatized Al K_α X-ray source (300 W, 5 mA, and 15 kV). All binding energies were calibrated using the C 1s level at 284.8 eV as reference. The N₂ adsorption-desorption isotherms were measured at 77 K (ASAP 2010) to obtain the porous structures and Brunauer-Emmett-Teller (BET) specific surface area. UV-vis spectroscopy was conducted in the wavelength range 200–800 nm using a Daojin UV-2550PC spectrometer equipping with an integrated sphere accessory. Photoluminescence (PL) spectra were recorded on a LS 50B spectrometer

(Perkin Elmer, Inc., USA) using an excitation wavelength of 230 nm at room temperature.

2.3. Photocatalytic hydrogen evolution

Photocatalytic H₂ evolution was performed in a 100-mL three-neck flat-bottom Pyrex flask at ambient pressure and room temperature. The reactor was sealed with a silicone rubber septum. A 300-W Xe lamp (PLS-SXE300, Beijing Perfect light Technology Co. Ltd. China) with a UV cut-off filter ($\lambda \geq 420$ nm) was used as the light source to trigger the photocatalytic reaction (light intensity of approx. 160 mW cm⁻²). In a typical experiment, photocatalyst powder (50 mg) was added to the reactor containing 0.25 mol L⁻¹ Na₂S–Na₂SO₃ aqueous solution (80 mL) under constant stirring and ultrasonication. Before the photocatalytic reaction, the suspension was bubbled with N₂ for 30 min to remove dissolved oxygen and ensure an anaerobic environment. After irradiation for 1 h, evolved gas (400 μ L) was collected through the silicone rubber septum and analyzed by gas chromatography (GC; GC-9560, TCD, with Ar as carrier gas). The photocatalytic reaction was then continued for a further 3 h.

2.4. Electrochemical tests

Working electrodes were prepared using a typical method: Photocatalyst powder (5 mg) and 0.25% Nafion solution (20 μ L) were added to absolute ethanol (2 mL), and the mixed solution was sonicated for 2 h. Next, a 500- μ L aliquot of the mixed solution was injected onto a fluorine-doped tin oxide (FTO) glass substrate (2×3.5 cm). The resulting electrodes were dried under an infrared lamp and calcined in a tube furnace at 150 °C for 1 h under a N₂ gas flow.

Transient photocurrent experiments were performed on an electrochemical analyzer (CHI-660, Chenhua, Shanghai) using a standard three-electrode cell at an initial voltage of 0.1 V vs. Ag/AgCl, the as-prepared working electrodes, Pt, and Ag/AgCl (saturated KCl) electrodes were used as the working, counter, reference electrodes, respectively. Na₂SO₄ aqueous solution (0.5 mol L⁻¹) was used as the electrolyte. A 300-W Xe arc lamp with a UV cut-off filter ($\lambda \geq 420$ nm) was used as the light source.

Electrochemical impedance spectroscopy (EIS) of the above-mentioned working electrodes in the three-electrode system was conducted using a computer-controlled IM6e impedance measurement unit (Zahner Elektrik, Germany) over a frequency range of 0.1–100 000 Hz with an ac signal amplitude of 5 mV in the dark. The mixed aqueous solution containing 0.1 mol L⁻¹ Na₂S and 0.02 mol L⁻¹ Na₂SO₃ was used as the electrolyte.

Electrocatalytic hydrogen evolution experiments were performed using a three-electrode cell. Linear sweep voltammetry with a scan rate of 5 mV⁻¹ was performed in a H₂SO₄ electrolyte solution (0.5 mol L⁻¹). Pt and Ag/AgCl (saturated KCl) were used as the counter and reference electrodes, respectively. The potential values were normalized to the reverse hydrogen electrode (RHE). In 0.5 mol L⁻¹ H₂SO₄ electrolyte solution, E(NHE) =

E(Al/AgCl) + 0.202 V. The working electrodes were prepared as follows: Photocatalyst (6 mg) was dispersed in deionized water (2 mL) by ultrasonication for at least 2 h. An aliquot of the dispersion (3 μ L) was then added onto a glassy carbon electrode. After drying, 0.5% Nafion solution containing 10 vol% ethanol (3 μ L) was injected on the top of the photocatalyst layer and dried under an infrared lamp.

3. Results and discussion

3.1. Structures and compositions of photocatalysts

XRD patterns were used to confirm the crystalline structure and phase purity of the as-prepared pure and composite photocatalysts. Fig. 1(A) shows powder XRD patterns of pure CdS NSs and composite CdS NSs with different NiS₂ and CB contents. According to the standard XRD pattern (JCPDS No. 41-1049), it was clear that the seven characteristic peaks located at approximately 25.11°, 26.82°, 28.2°, 36.6°, 43.7°, 47.8°, and 52.16°, were consistent with the (100), (002), (101), (102), (110), (103), and (112) diffraction planes of hexagonal CdS, respectively [44]. No additional diffraction peaks were observed for the CdS NSs, showing that the as-synthesized CdS NSs were well crystallized. Compared with the XRD pattern of pure CdS, four typical diffraction peaks were detected in the XRD pattern of CdS-5%NiS₂ (Fig. 1(B)). The four peaks located at 31.5°, 35.3°, 38.8°, and 53.5° were well indexed to the (200), (210), (211), and (311) planes of pyrite-type NiS₂ (JCPDS No. 89-1495) [59]. Furthermore, no diffraction peaks of NiS₂ and CB were detected in the XRD patterns of the CdS/CB/NiS₂ ternary hybrid photocatalysts, which might be due to the low contents and high dispersion of NiS₂ and CB in these composites. The existence of NiS₂ and CB in the CdS/CB/NiS₂ composite photocatalysts required further confirmation by TEM and XPS analysis.

TEM and HRTEM were used to investigate the morphology and microstructure of the as-prepared CdS NSs and their composites. The compositional distribution of chemical elements in CdS-0.5%CB-1.0%NiS₂ was confirmed by energy dispersive X-ray (EDX) spectroscopy mapping measurements. As shown in Fig. 2(A) and (B), CdS NSs had lateral dimensions of 200–400

nm and near-transparent flower features, which further indicated their ultrathin nanosheet microstructure, in agreement with previous reports [45]. Compared with Fig. 2(A) and (B), Fig. 2(C) clearly showed that some CB and NiS₂ nanoparticles were dispersed uniformly on the surface of CdS-0.5%CB-1.0%NiS₂, in good agreement with previously reported work [58,64]. Further observation showed that the lateral diameters of the CB nanoparticles and NiS₂ were about 30 and 50 nm, respectively. It is well known that an intimate contact interface can provide photogenerated charge transfer and trapping channels to achieve rapid separation. Furthermore, as shown in Fig. 2(D), the HRTEM image of CdS-0.5%CB-1.0%NiS₂ exhibited clear lattice fringes with interplanar spacings of 0.33 and 0.284 nm, corresponding to the (002) and (200) planes of hexagonal CdS (JCPDS No. 41-1049) and NiS₂ (JCPDS No. 89-1495), respectively. As shown in Fig. 2(K), EDX peaks of C, Cd, Ni, and S elements were detected in the CdS-0.5%CB-1.0%NiS₂ composite, further evidencing the presence of CB and NiS₂. The coexistence of C, Cd, Ni, and S elements in CdS-0.5%CB-1.0%NiS₂ was also confirmed by HRTEM elemental mapping measurements (Fig. 2(E)–(J)). All results indicated that the CdS-0.5%CB-1.0%NiS₂ ternary composite photocatalysts were successfully synthesized by the two-step solvothermal/impregnation method, as demonstrated in the above XRD patterns.

The elemental composition and oxidation states of the ternary CdS-0.5%CB-1.0%NiS₂ composite were further analyzed by XPS. As shown in Fig. 3(A), the full survey scan XPS spectrum confirmed the presence of C, Cd, Ni, and S elements in the CdS-0.5%CB-1.0%NiS₂ composite. The corresponding XPS spectra of C 1s, Cd 3d, Ni 2p, and S 2p of the CdS-0.5%CB-1.0%NiS₂ composite are shown in Fig. 3(B)–(E), respectively. The C 1s XPS spectrum was divided into two peaks (Fig. 3(B)) at 284.6 eV, which could be assigned to the unavoidable adventitious carbon and loaded graphitic carbon (C–C bonds) on the sample surface, and at 286.2 eV, which might originate from absorbed gaseous molecules (C–O bonds). In Fig. 3(C), Cd 3d_{5/2} and Cd 3d_{3/2} XPS peaks were observed at 405 and 411.8 eV with a peak separation of 6.8 eV, in good agreement with those reported for CdS NSs [65]. The XPS peaks of the Ni 2p spectrum located at 856.1 (Ni 2p_{3/2}) and 861.8 eV (Ni 2p_{3/2} satellite),

Fig. 1. (A) XRD patterns of pure CdS NSs and composite CdS NSs with different NiS₂ and CB contents; (B) XRD patterns of composite CdS NSs with different NiS₂ contents.

Fig. 2. TEM images of CdS NSs (A, B) and CdS-0.5%CB-1.0%NiS₂ (C). (D) HRTEM image of CdS-0.5%CB-1.0%NiS₂. Elemental mapping (E–J) and EDX spectrum (K) of CdS-0.5%CB-1.0%NiS₂.

correspond to the dominant oxidation state of Ni²⁺ [59]. Additionally, S 2*p* peaks were located at 161.6 and 160.4 eV with a spin-orbit separation of 1.2 eV, corresponding to sulfide in CdS NSs and NiS₂ cocatalysts [58,66]. The Ni 2*p* and S 2*p* XPS spectra further indicated the presence of a pure NiS₂ phase in the CdS-0.5%CB-1.0%NiS₂ composite.

The porous structures and surface area of these composite nanostructures were further investigated using N₂ adsorption-desorption isotherms. Fig. 4 shows the nitrogen adsorption-desorption isotherms and corresponding pore size distribution curves of CdS NSs, CdS-1%NiS₂, and CdS-0.5%CB-1%NiS₂. All three samples clearly showed type-IV adsorption-desorption isotherms with a distinct H3 hysteresis loop (relative pressure range of 0–1) according to the Brunauer-Deming-Deming-Teller classification, indicating typical mesoporous structures with slit-like pores. As shown in the inset of Fig. 4, the corresponding pore size distribution curves of the three samples exhibited sharp peaks located at approximately 2–30 nm, further confirming the presence of mesopores. The obtained BET specific surface area, pore volume, and average pore diameter of these samples are shown in Table 1. All samples exhibited mean pore diameters between 5 and 15 nm, suggesting mesoporous structures. The surface area (78.2557 m² g⁻¹) and pore volume (0.181855 cm³ g⁻¹) of

CdS-0.5%CB-1%NiS₂ were much smaller than those of pure CdS NSs (94.5692 m² g⁻¹ and 0.339241 cm³ g⁻¹, respectively), which might be due to the partially filled mesopores of pure CdS NSs by NiS₂ loading. These results clearly indicated that increased active sites and charge separation, rather than the surface area, should be crucial factors determining photocatalytic H₂ evolution.

3.2. Optical properties of photocatalysts

The optical absorption spectra of pure CdS NSs and the CdS/CB/NiS₂ composite photocatalysts were also recorded using UV-vis diffuse reflectance spectroscopy. UV-vis absorption spectra and Tauc plots of the as-prepared photocatalysts are shown in Fig. 5. The as-prepared CdS NSs exhibited strong visible light absorption with edges at around 550 nm, corresponding to the intrinsic band gap of pure CdS. After loading cocatalysts on CdS NSs, the resultant ternary CdS/CB/NiS₂ and binary CdS-1%NiS₂ composites showed obvious red shifts and enhanced absorption in the visible light range. In particular, compared with CdS-1.0%NiS₂, significantly enhanced photoabsorption was observed for the ternary CdS/CB/NiS₂ composites in the visible region of 550–800 nm. The enhanced photoabsorption intensities of the ternary composites could be

Fig. 3. XPS spectra of CdS-0.5%CB-1.0%NiS₂.

attributed to carbon layer insertion between the CdS NSs photocatalyst and NiS₂ cocatalysts, which could decrease light reflection and accelerate electron transition, and, therefore, favor photocatalytic H₂ evolution. The band gaps of CdS NSs and the composite photocatalysts could be calculated using the equation [41] $\alpha = A(h\nu - E_g)^{n/2}/h\nu$, where α , A , h , ν , and E_g are the absorption coefficient, proportionality constant, Planck's constant, frequency of incident light, and band energy, respectively. The n value is equal to 1, which was mainly dependent on the optical transition type of the semiconductors. The band gap energies of samples could be observed by intercepting the tangents on a horizontal axis in the corresponding Tauc plots of the UV-vis spectra (Fig. 5(B)). The band gap for pure CdS NSs was about 2.33 eV, which was consistent with the reported value [45]. The corresponding band gaps of CdS-1%NiS₂ and CdS-0.5%CB-1%NiS₂ were estimated to be 2.17 and 2.02 eV,

respectively. All results suggested that the co-loading of CB and NiS₂ could narrow the band energy of the CdS NSs and enhance visible-light absorption to facilitate the enhanced photocatalytic H₂ evolution.

3.3. Activities and stabilities of photocatalysts

The photocatalytic H₂ evolution of pure CdS NSs and different composite photocatalysts was evaluated under visible light irradiation ($\lambda \geq 420$ nm) using 0.25 mol L⁻¹ Na₂S-Na₂SO₃ aqueous solution as a sacrificial reagent. No appreciable hydrogen evolution was detected in the blank experiments, suggesting that hydrogen was mainly produced via a photocatalytic process. As shown in Fig. 6(A), time-dependent H₂ evolution over the as-obtained photocatalysts showed a significant linear increase throughout the photocatalytic reactions, which implied that the as-prepared samples were relatively stable under visible-light irradiation. The average H₂-evolution rates of all photocatalyst samples throughout the reactions were calculated, as shown in Fig. 6(B). Interestingly, the as-synthesized CdS NSs exhibited much better photocatalytic H₂-evolution activity than previously reported CdS nanoparticles and nanorods [67,68]. The CdS/CB/NiS₂ composite photocatalysts exhibited much higher rates of H₂ evolution than that of pure CdS NSs. The optimum loading contents of CB and NiS₂ on the CdS NS surfaces were found to be about 0.5 and 1 wt%, respectively.

Fig. 4. N₂ adsorption-desorption isotherms and corresponding pore size distribution curves (inset) of pure CdS NSs, CdS-1%NiS₂, and CdS-0.5%CB-1%NiS₂.

Table 1

Pore structure parameters of pure CdS NSs, CdS-1%NiS₂, and CdS-0.5%CB-1%NiS₂.

Photocatalyst	BET surface area (m ² g ⁻¹)	Mean pore diameter (nm)	Pore volume (cm ³ g ⁻¹)
CdS NSs	94.5692	11.0709	0.339241
CdS-1%NiS ₂	100.4677	6.9065	0.213831
CdS-0.5%CB-1%NiS ₂	78.2557	7.3298	0.181855

Fig. 5. (A) UV-vis absorption spectra of as-prepared samples; (B) Tauc plots of the UV-vis spectra.

Fig. 6. Time-dependent (A) and average H₂ evolution rates (B) over different photocatalysts in 0.25 mol L⁻¹ Na₂S–Na₂SO₃ aqueous solution. (a) CdS NSs; (b) CdS–1%NiS₂; (c) CdS–0.5%CB; (d) CdS–0.5%CB–1%NiS₂; (e) CdS–1%CB–1%NiS₂; (f) CdS–1.5%CB–1%NiS₂; (g) CdS–2%CB–1%NiS₂; (h) CdS–1%Pt. Reaction conditions: catalyst 50 mg, 0.25 mol L⁻¹ Na₂S–Na₂SO₃ aqueous solution 80 mL, light source, xenon lamp (300 W) with a UV cut-off filter ($\lambda \geq 420$ nm).

Under the optimized conditions, the CdS–0.5%CB–1%NiS₂ photocatalyst could reach a highest H₂ evolution rate of 166.7 μmol h⁻¹, which was about 5.16 and 1.87 times higher than those of pure CdS NSs (32.3 μmol h⁻¹) and CdS–1.0% NiS₂ (89.3 μmol h⁻¹), respectively. This suggested that the metallic interfacial layer of CB greatly improved the photocatalytic H₂-evolution activity of the binary CdS–NiS₂ composite. However, the photocatalytic H₂-evolution activity of CdS–0.5%CB–1%NiS₂ was still lower than that of CdS–1%Pt, implying that interfacial contact between the cocatalysts and CdS NSs could be further improved. The clear decrease in photocatalytic H₂-evolution of CdS NSs with increasing CB loading content could be attributed to light shielding and scattering effects, which would reduce the visible light utilization efficiency. These results indicated that loading suitable contents of CB and NiS₂ on the surface of CdS NSs could significantly enhance the photocatalytic H₂-evolution activity of CdS NSs, and that an excellent synergetic effect between CB and NiS₂ could effectively improve visible light absorption, promote the separation of photogenerated electron–hole pairs, and boost the H₂-evolution kinetics.

To better evaluate the long-term stability and reproducibility of the CdS/CB/NiS₂ composites, CdS–0.5%CB–1% NiS₂ and pure CdS NSs were recycled in photocatalytic H₂ evolution performed 3 h as one cycle. After each cycle, the photocatalytic

reaction system was evacuated. As shown in Fig. 7, an obvious activity loss (almost 50%) was observed for pure CdS NSs after four consecutive reaction cycles under visible light irradiation, which might be attributed to the rapid recombination of photogenerated charge carriers and strong photocorrosion of the CdS NSs. Compared with pure CdS NSs, CdS–0.5%CB–1%NiS₂ exhibited much better long-term stability and reproducibility

Fig. 7. Repeated photocatalytic H₂ evolution over CdS–0.5%CB–1%NiS₂ and pure CdS NSs in 0.25 mol L⁻¹ Na₂S–Na₂SO₃ aqueous solution.

(about 20% activity loss). All results suggested that loading CB and NiS₂ onto the surface of CdS NSs could partially reduce CdS NS photocorrosion, which favors its application in sustainable reuse.

3.4. Charge-separation performance and proposed mechanism

The charge separation and electronic transition behavior of the as-prepared samples were further assessed using PL emission spectra. PL spectra are widely utilized to analyze the recombination rate of photogenerated electron-hole pairs in photoexcited semiconductors [69]. The PL spectra of pure CdS NSs, CdS-1%NiS₂, and CdS-0.5%CB-1%NiS₂ were performed with an excitation wavelength of 230 nm at room temperature. As shown in Fig. 8(A), the emission peak intensity of CdS-0.5%CB-1%NiS₂ was much lower than that of pure CdS NSs and CdS-1%NiS₂. These results suggested that the recombination rate of the photogenerated electron-hole pairs could be efficiently suppressed under visible light due to the co-loading of CB and NiS₂. This further indicated the improved separation and transfer efficiency of photo-excited charge carriers. The PL spectra intensities of pure CdS NSs, CdS-1%NiS₂, and CdS-0.5%CB-1%NiS₂ photocatalysts were in good agreement with their corresponding photocatalytic activities, confirming the key roles of charge separation and transfer in boosting H₂ evolution.

The separation efficiency of photogenerated charge carriers of pure CdS NSs, CdS-1%NiS₂ and CdS-0.5%CB-1%NiS₂ photocatalysts were further characterized by photoelectrochemical

(PEC) analysis. The transient photocurrent response (*I*-*t* curves) was measured in 0.1 mol L⁻¹ Na₂SO₄ aqueous solution at 0.1 V vs. Ag/AgCl for several visible light on-off cycles. As shown in Fig. 8(B), the photocurrent density of CdS-0.5%CB-1%NiS₂ composite was much higher than that of pure CdS NSs, suggesting that a higher interfacial separation efficiency of photogenerated charge carriers was achieved after loading CB and NiS₂ on the surface of CdS NSs. Interestingly, CdS-0.5%CB-1%NiS₂ exhibited a much higher photocurrent density than CdS-1%NiS₂, indicating that the CB cocatalyst played an important role in enhancing the interfacial charge transfer. These results further demonstrated that the co-loading of CB and NiS₂ on the surface of CdS NSs could greatly promote the photocatalytic performance by improving photogenerated charge transfer and the separation efficiency. Consequently, more photo-generated electrons could be separated and transferred to drive H₂ generation.

EIS is a valid tool for investigating the separation efficiency of photogenerated electron-hole pairs and electron transfer resistance at solid/electrolyte interfaces [70,71]. Nyquist plots of the three photocatalyst samples were recorded in the dark using Na₂S-Na₂SO₃ aqueous solution as the electrolyte (Fig. 8(C)). The semicircle radius of the CdS-0.5%CB-1%NiS₂ composites was much smaller than those of pure CdS NSs and binary CdS-1%NiS₂, indicating that loading suitable contents of CB and NiS₂ on the CdS NSs could effectively reduce the interface charge transfer resistance and promote the separation and transfer of photogenerated charge carriers.

Polarization curves were employed to further identify the

Fig. 8. PL spectra (A), photocurrent response (B), EIS spectra (C), and polarization curves (D) of pure CdS NSs, CdS-1%NiS₂, and CdS-0.5%CB-1%NiS₂.

enhanced surface H_2 evolution kinetics [72]. As shown in Fig. 8(D), the cathodic current observed from 0 to -1.2 V vs. NHE could be attributed to electrocatalytic H_2 evolution, indicating that coloading CB and NiS_2 on CdS NSs could significantly decrease the electrocatalytic H_2 -evolution overpotential. $CdS-0.5\%CB-1\%NiS_2$ showed a much lower electrocatalytic H_2 -evolution overpotential than those of pure CdS and $CdS-1\%NiS_2$. These results further suggested that CB played a positive role in efficiently boosting the electrocatalytic H_2 -evolution kinetics and decreasing the overpotential in 0.5 mol L^{-1} H_2SO_4 solution. According to the photocatalytic mechanism, CB acted not only as a cocatalysts for H_2 evolution, but also as a conductive electron bridge, to directly enhance photocatalytic H_2 evolution.

Based on the above results, a possible reaction mechanism for photocatalytic H_2 evolution and the interface charge transfer over the $CdS/CB/NiS_2$ composites under visible light irradiation were proposed, as shown in Scheme 2. Under visible light irradiation, the electrons are excited from the valence band to the conduction band of CdS NSs, leading to the production of photogenerated electron-hole pairs. Only a small fraction of electrons can react with H^+ ions to form H_2 , because of the rapid recombination of photogenerated electron-hole pairs in CdS NSs without cocatalysts loading, leading to their relatively low activity toward photocatalytic H_2 evolution. In contrast, when inserting the conductive CB layer between the CdS NS photocatalyst and NiS_2 cocatalyst, the photogenerated electrons can first transfer to CB due to its intimate interface contact and matching work function. Then, CB can work as an electron mediator to transfer the collected electrons to the H_2 -evolution active sites on NiS_2 owing to its excellent electrical conductivity and carrier mobility properties, leading to the effective separation and transfer of the photogenerated electron-hole pairs. Therefore, the ternary $CdS/CB/NiS_2$ composite photocatalysts exhibited much better photocatalytic H_2 -evolution activity than the binary CdS/NiS_2 composite. Meanwhile, holes with strong oxidation abilities on the valence band of CdS NSs could be rapidly removed by Na_2S/Na_2SO_3 , which further improves the

photocatalytic H_2 -evolution activity. In summary, the excellent synergetic effect between CB and NiS_2 can effectively promote the separation of photogenerated electron-hole pairs and boost the H_2 -evolution kinetics to achieve a significant enhancement in photocatalytic H_2 -evolution activity over the $CdS/CB/NiS_2$ composite photocatalysts.

4. Conclusions

CdS NS photocatalysts modified by dual earth-abundant cocatalysts CB and NiS_2 were successfully synthesized via a two-step solvothermal/impregnation method. All experimental results showed that the as-prepared $CdS-0.5\%CB-1\%NiS_2$ composite photocatalyst exhibited the highest photocatalytic H_2 -evolution rate of $166.7 \mu mol h^{-1}$ in 0.25 mol L^{-1} $Na_2S-Na_2SO_3$ aqueous solution under visible-light irradiation, which could be attributed to the excellent synergetic effect between CB and NiS_2 as dual cocatalysts on the surface of CdS NSs. Inserting the carbon layer between the CdS NS photocatalyst and NiS_2 cocatalyst is thought to effectively increase visible-light absorption, promote the separation and transportation of charge carriers, and accelerate the surface water reduction kinetics to achieve an obvious enhancement in H_2 evolution activity. The present study indicates that CB and NiS_2 as dual cocatalysts show potential for enhancing visible light photocatalytic H_2 evolution. This work also provides new insight into the construction of highly efficient and stable CdS NS-based hybrid photocatalysts with dual earth-abundant cocatalysts for photocatalytic applications.

References

- [1] J. X. Low, J. G. Yu, M. Jaroniec, S. Wageh, A. A. Al-Ghamdi, *Adv. Mater.*, **2017**, 29, 1601694.
- [2] X. Li, J. G. Yu, J. X. Low, Y. P. Fang, J. Xiao, X. B. Chen, *J. Mater. Chem. A*, **2015**, 3, 2485–2534.
- [3] A. Fujishima, K. Honda, *Nature*, **1972**, 238, 37–38.
- [4] T. T. Wu, X. D. Kang, M. W. Kadi, I. Ismail, G. Liu, H. M. Cheng, *Chin. J. Catal.*, **2015**, 36, 2103–2108.
- [5] Y. X. Liu, Z. L. Wang, W. X. Huang, *Appl. Surf. Sci.*, **2016**, 389, 760–767.
- [6] J. Q. Wen, X. Li, W. Liu, Y. P. Fang, J. Xie, Y. H. Xu, *Chin. J. Catal.*, **2015**, 36, 2049–2070.
- [7] Q. Q. Hu, J. Q. Huang, G. J. Li, Y. B. Jiang, H. Lan, W. Guo, Y. G. Cao, *Appl. Surf. Sci.*, **2016**, 382, 170–177.
- [8] W. J. Dai, J. Q. Yan, K. Dai, L. D. Li, N. J. Guan, *Chin. J. Catal.*, **2015**, 36, 1968–1975.
- [9] Q. Li, B. D. Guo, J. G. Yu, J. R. Ran, B. H. Zhang, H. J. Yan, J. R. Gong, *J. Am. Chem. Soc.*, **2011**, 133, 10878–10884.
- [10] Y. Peng, L. Shang, Y. T. Cao, Q. Wang, Y. F. Zhao, C. Zhou, T. Bian, L. Z. Wu, C. H. Tung, T. R. Zhang, *Appl. Surf. Sci.*, **2015**, 358, 485–490.
- [11] S. Ma, J. Xie, J. Q. Wen, K. L. He, X. Li, W. Liu, X. C. Zhang, *Appl. Surf. Sci.*, **2017**, 391, 580–591.
- [12] G. Hitoki, A. Ishikawa, T. Takata, J. N. Kondo, M. Hara, K. Domen, *Chem. Lett.*, **2002**, 31, 736–737.
- [13] L. J. Shen, R. W. Liang, L. Wu, *Chin. J. Catal.*, **2015**, 36, 2071–2088.
- [14] M. S. Akple, J. Low, S. Wageh, A. A. Al-Ghamdi, J. G. Yu, J. Zhang, *Appl. Surf. Sci.*, **2015**, 358, 196–203.
- [15] Y. J. Cui, Y. X. Wang, H. Wang, F. Cao, F. Y. Chen, *Chin. J. Catal.*, **2016**,

Scheme 2. Proposed photocatalytic H_2 evolution and charge transfer mechanisms of $CdS/CB/NiS_2$ composite photocatalysts under visible-light irradiation.

Graphical Abstract

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Improved visible-light photocatalytic H₂ generation over CdS nanosheets decorated by NiS₂ and metallic carbon black as dual earth-abundant cocatalysts

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The as-prepared CdS/CB/NiS₂ composite photocatalysts exhibited better photocatalytic H₂-evolution performance under visible-light irradiation, which could due to the excellent synergetic effect between the CB and NiS₂ as dual co-catalysts on the surface of CdS nanosheets.

- 37, 1899–1906.
- [16] K. L. He, J. Xie, X. Y. Luo, J. Q. Wen, S. Ma, X. Li, Y. P. Fang, X. C. Zhang, *Chin. J. Catal.*, **2017**, 38, 240–252.
 - [17] Z. Z. Lin, L. H. Lin, X. C. Wang, *Chin. J. Catal.*, **2015**, 36, 2089–2094.
 - [18] J. Q. Wen, J. Xie, X. B. Chen, X. Li, *Appl. Surf. Sci.*, **2017**, 391, 72–123.
 - [19] J. F. Zhang, S. Wageh, A. Al-Ghamdi, J. G. Yu, *Appl. Catal. B*, **2016**, 192, 101–107.
 - [20] Q. Li, X. Li, S. Wageh, A. A. Al-Ghamdi, J. Yu, *Adv. Energy Mater.*, **2015**, 5, 1500010.
 - [21] H. Du, Y. N. Liu, C. C. Shen, A. W. Xu, *Chin. J. Catal.*, **2017**, 38, 1295–1306.
 - [22] Q. J. Xiang, B. Cheng, J. G. Yu, *Appl. Catal. B*, **2013**, 138, 299–303.
 - [23] J. G. Yu, Y. F. Yu, P. Zhou, W. Xiao, B. Cheng, *Appl. Catal. B*, **2014**, 156, 184–191.
 - [24] D. Zhao, Q. Wu, C. F. Yang, R. T. Koodali, *Appl. Surf. Sci.*, **2015**, 356, 308–316.
 - [25] X. Li, J. G. Yu, M. Jaroniec, *Chem. Soc. Rev.*, **2016**, 45, 2603–2636.
 - [26] H. G. Yu, F. Y. Chen, F. Chen, X. F. Wang, *Appl. Surf. Sci.*, **2015**, 358, 385–392.
 - [27] J. J. Zhou, R. Wang, X. L. Liu, F. M. Peng, C. H. Li, F. Teng, Y. P. Yuan, *Appl. Surf. Sci.*, **2015**, 346, 278–283.
 - [28] Y. J. Cui, *Chin. J. Catal.*, **2015**, 36, 372–379.
 - [29] J. Z. Su, T. Zhang, L. Wang, J. W. Shi, Y. B. Chen, *Chin. J. Catal.*, **2017**, 38, 489–497.
 - [30] L. J. Zhang, S. Li, B. K. Liu, D. J. Wang, T. F. Xie, *ACS Catal.*, **2014**, 4, 3724–3729.
 - [31] L. Zou, H. R. Wang, X. Wang, *ACS Sustain. Chem. Eng.*, **2016**, 5, 303–309.
 - [32] X. L. Yin, J. Liu, W. J. Jiang, X. Zhang, J. S. Hu, L. J. Wan, *Chem. Commun.*, **2015**, 51, 13842–13845.
 - [33] Q. Li, H. Meng, P. Zhou, Y. Q. Zheng, J. Wang, J. G. Yu, J. R. Gong, *ACS Catal.*, **2013**, 3, 882–889.
 - [34] J. Zhang, F. Huang, *Appl. Surf. Sci.*, **2015**, 358, 287–295.
 - [35] Q. L. Xu, B. Cheng, J. Yu, G. Liu, *Carbon*, **2017**, 118, 241–249.
 - [36] X. Li, R. C. Shen, S. Ma, X. B. Chen, J. Xie, *Appl. Surf. Sci.*, **2018**, 430, 53–107.
 - [37] X. Li, J. G. Yu, S. Wageh, A. A. Al-Ghamdi, J. Xie, *Small*, **2016**, 12, 6640–6696.
 - [38] Y. Xu, R. Xu, *Appl. Surf. Sci.*, **2015**, 351, 779–793.
 - [39] T. M. Di, B. C. Zhu, J. Zhang, B. Cheng, J. G. Yu, *Appl. Surf. Sci.*, **2016**, 389, 775–782.
 - [40] S. W. Cao, Y. P. Yuan, J. Fang, M. M. Shahjamali, F. Y. C. Boey, J. Barber, S. C. Joachim Loo, C. Xue, *Int. J. Hydrogen Energy*, **2013**, 38, 1258–1266.
 - [41] J. L. Yuan, J. Q. Wen, Q. Z. Gao, S. C. Chen, J. M. Li, X. Li, Y. P. Fang, *Dalton Trans.*, **2015**, 44, 1680–1689.
 - [42] J. Zhang, S. Z. Qiao, L. Qi, J. G. Yu, *Phys. Chem. Chem. Phys.*, **2013**, 15, 12088–12094.
 - [43] J. Jin, J. G. Yu, D. P. Guo, C. Cui, W. Ho, *Small*, **2015**, 11, 5262–5271.
 - [44] Y. Xu, W. W. Zhao, R. Xu, Y. M. Shi, B. Zhang, *Chem. Commun.*, **2013**, 49, 9803–9805.
 - [45] S. Iqbal, Z. W. Pan, K. B. Zhou, *Nanoscale*, **2017**, 9, 6638–6642.
 - [46] H. J. Yan, J. H. Yang, G. J. Ma, G. P. Wu, X. Zong, Z. B. Lei, J. X. Shi, C. Li, *J. Catal.*, **2009**, 266, 165–168.
 - [47] R. B. Wei, P. Y. Kuang, H. Cheng, Y. B. Chen, J. Y. Long, M. Y. Zhang, Z. Q. Liu, *ACS Sustain. Chem. Eng.*, **2017**, 5, 4249–4257.
 - [48] P. Y. Kuang, P. X. Zheng, Z. Q. Liu, J. L. Lei, H. Wu, N. Li, T. Y. Ma, *Small*, **2016**, 12, 6735–6744.
 - [49] K. Chang, M. Li, T. Wang, S. Ouyang, P. Li, L. Liu, J. Ye, *Adv. Energy Mater.*, **2015**, 5, 1402279.
 - [50] Q. J. Xiang, F. Y. Cheng, D. Lang, *ChemSusChem*, **2016**, 9, 996–1002.
 - [51] X. Zong, J. F. Han, G. J. Ma, H. J. Yan, G. P. Wu, C. Li, *J. Phys. Chem. C*, **2011**, 115, 12202–12208.
 - [52] W. Zhang, Y. B. Wang, Z. Wang, Z. Y. Zhong, R. Xu, *Chem. Commun.*, **2010**, 46, 7631–7633.
 - [53] Y. X. Pan, T. H. Zhou, J. Y. Han, J. D. Hong, Y. B. Wang, W. Zhang, R. Xu, *Catal. Sci. Technol.*, **2016**, 6, 2206–2213.
 - [54] F. Y. Cheng, Q. J. Xiang, *RSC Adv.*, **2016**, 6, 76269–76272.
 - [55] H. G. Yu, X. Huang, P. Wang, J. G. Yu, *J. Phys. Chem. C*, **2016**, 120, 3722–3730.
 - [56] D. Lang, F. Y. Cheng, Q. J. Xiang, *Catal. Sci. Technol.*, **2016**, 6, 6207–6216.

- [57] Y. P. Yuan, S. W. Cao, L. S. Yin, L. Xu, C. Xue, *Int. J. Hydrogen Energy*, **2013**, 38, 7218–7223.
- [58] L. S. Yin, Y. P. Yuan, S. W. Cao, Z. Zhang, C. Xue, *RSC Adv.*, **2014**, 4, 6127.
- [59] F. Chen, H. Yang, X. F. Wang, H. G. Yu, *Chin. J. Catal.*, **2017**, 38, 296–304.
- [60] H. Pang, C. Z. Wei, X. X. Li, G. C. Li, Y. H. Ma, S. J. Li, J. Chen, J. S. Zhang, *Sci. Rep.*, **2014**, 4, 3577.
- [61] J. Q. Wen, J. Xie, Z. H. Yang, R. C. Shen, H. Y. Li, X. Y. Luo, X. B. Chen, X. Li, *ACS Sustain. Chem. Eng.*, **2017**, 5, 2224–2236.
- [62] J. Q. Wen, X. Li, H. Q. Li, S. Ma, K. L. He, Y. Xu, Y. H. Fang, W. Liu, Q. Z. Gao, *Appl. Surf. Sci.*, **2015**, 358, 204–212.
- [63] G. C. Bi, J. Q. Wen, X. Li, W. Liu, J. Xie, Y. P. Fang, W. W. Zhang, *RSC Adv.*, **2016**, 6, 31497–31506.
- [64] J. Wen, X. Li, H. Li, S. Ma, K. He, Y. Xu, Y. Fang, W. Liu, Q. Gao, *Appl. Surf. Sci.*, **2015**, 358, 204–212.
- [65] M. Zhukovskiy, P. Tongying, H. Yashan, Y. X. Wang, M. Kuno, *ACS Catal.*, **2015**, 5, 6615–6623.
- [66] J. He, L. Chen, Z. Q. Yi, C. T. Au, S. F. Yin, *Ind. Eng. Chem. Res.*, **2016**, 55, 8327–8333.
- [67] N. Zhang, Y. H. Zhang, X. Y. Pan, X. Z. Fu, S. Q. Liu, Y. J. Xu, *J. Phys. Chem. C*, **2011**, 115, 23501–23511.
- [68] X. L. Yin, L. L. Li, W. J. Jiang, Y. Zhang, X. Zhang, L. J. Wan, J. S. Hu, *ACS Appl. Mater. Interfaces*, **2016**, 8, 15258–15266.
- [69] S. Zou, Z. H. Fu, C. Xiang, W. F. Wu, S. P. Tang, Y. C. Liu, D. L. Yin, *Chin. J. Catal.*, **2015**, 36, 1077–1085.
- [70] M. S. Akple, J. X. Low, Z. Y. Qin, S. Wageh, A. A. Al-Ghamdi, J. G. Yu, S. W. Liu, *Chin. J. Catal.*, **2015**, 36, 2127–2134.
- [71] K. L. He, J. Xie, Z. H. Yang, R. C. Shen, Y. P. Fang, S. Ma, X. B. Chen, X. Li, *Catal. Sci. Technol.*, **2017**, 7, 1193–1202.
- [72] J. Q. Wen, J. Xie, H. D. Zhang, A. P. Zhang, Y. J. Liu, X. B. Chen, X. Li, *ACS Appl. Mater. Interfaces*, **2017**, 9, 14031–14042.

利用地球上丰富的炭黑和NiS₂双助催化剂修饰提高CdS纳米片体系的可见光产氢活性

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摘要: 光催化产氢技术是目前解决能源和环境问题的最有潜力的方法之一, 因此制备安全高效的光催化剂已成为目前的研究热点。在目前研究的各种光催化剂中, CdS光催化剂因为具有较窄的带隙(2.4 eV)和合适的导带位置, 所以在可见光催化产氢领域受到广泛关注。然而, 光生电子/空穴对易复合和光腐蚀作用极大地限制了CdS光催化剂的放大应用。因此, 人们采用众多改性策略以提高CdS光催化剂的可见光产氢活性, 其中构建CdS纳米结构和负载助催化剂被认为是最有效的方式。构建CdS纳米结构既可以缩短载流子的迁移路径, 也可以减少CdS晶体中的缺陷。很多不同纳米结构的CdS光催化剂已经被开发, 例如纳米线、纳米颗粒和纳米棒等。因为制备过程极为复杂繁琐, 所以CdS纳米片的研究鲜见报道。

本文采用乙酸镉和硫脲为原材料, 通过简单的溶剂热法合成了CdS纳米片。在CdS的各类助催化剂中, 由于常用的Pt, Ag和Au等贵金属的高成本和低储量等问题严重限制了它们的实际应用, 所以近年来众多非贵金属助催化剂(例如MoS₂, WS₂, NiS, NiO和WC等)得到了广泛关注。由于非贵金属助催化剂存在弱电导率和低功函数等问题, 影响了对光生电子的收集和利用。纳米碳材料具有极高的电导率、强可见光吸收、有效的载流子分离和较多的反应位点等优点, 因此组合纳米碳材料和非贵金属助催化剂被认为是一种有效的解决方案。本文首次采用炭黑和NiS₂作为双助催化剂改性CdS纳米片, 通过简单的溶剂热/沉淀两步法成功合成了廉价高效的CdS/CB/NiS₂三元光催化体系。光催化产氢性能测试表明, CdS-0.5%CB-1%NiS₂展现出最高的光催化效率(166.7 μmol h⁻¹), 分别是CdS NSs和CdS-1.0%NiS₂的5.16和1.87倍。X射线衍射、高分辨电子显微镜和X射线光电子能谱结果证实了CdS催化剂的片状结构, 且炭黑和NiS₂成功负载在CdS纳米片表面。紫外-可见漫反射结果表明, 随着炭黑和NiS₂的负载, 复合催化剂的吸收边缘产生明显的红移, 且对可见光的吸收增强。荧光光谱、阻抗和瞬态光电流曲线测试结果证明, 炭黑和NiS₂的加入可以有效地促进光生电子/空穴对分离。极化曲线结果表明, 加入炭黑和NiS₂可以降低CdS的产氢过电势, 因此加速表面产氢动力学。总之, 炭黑和NiS₂之间显著的协同效应极大地提高了可见光吸收, 促进光生电子/空穴对分离, 加速表面产氢动力学, 最终得到了三元光催化体系极高的光催化产氢活性。

关键词: 光催化产氢; CdS纳米片; 炭黑; NiS₂; 双助催化剂

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