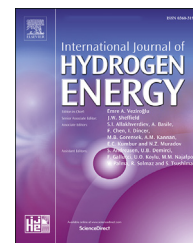


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Preparation of CdS-CoS_x photocatalysts and their photocatalytic and photoelectrochemical characteristics for hydrogen production

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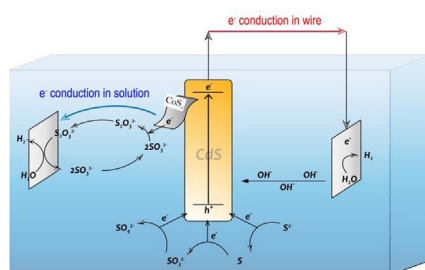
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HIGHLIGHTS

- CoS_x as co-catalyst is loaded on CdS nanorod by a facile method.
- CdS-CoS_x has good activity and stability for photoelectrochemical (PEC) reaction.
- PEC activity of CdS-CoS_x as photoanode for H₂ production is the same as that of CdS–Pt.
- An abnormal relationship between photocurrent and hydrogen production is found.
- The reaction network in Na₂S–Na₂SO₃ system for PEC H₂ production is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

A facile method of loading CoS_x nanosheet onto CdS nanorod has been designed, and the prepared CdS-CoS_x composite catalyst exhibited significantly improved performance for photocatalytic hydrogen evolution compared with CdS catalyst. This composite catalyst was also used as a photoanode for photoelectrochemical (PEC) hydrogen production. The hydrogen production rate reached 168.6 μmol cm⁻² h⁻¹ (37.77 L m⁻² h⁻¹) under the simulated solar light, which is 2.7 times that of CdS and the same as that of CdS–Pt. In addition, in the Na₂S–Na₂SO₃ system for PEC hydrogen production, an abnormal relationship between photocurrent and the hydrogen production yield was found. By designing a series of experiments, the photocatalytic and photoelectrochemical characteristics for hydrogen production were reasonably revealed for the first time. In this work, the prepared

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Photoelectrochemical hydrogen
production
Cobalt sulfide
Cadmium sulfide

structured catalyst is easy to be recycled, and CoS_x can replace precious metal Pt, showing a promising application.

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Introduction

Due to the exhaustion of non-renewable resources such as fossil fuels and increasingly serious environmental pollution, the search for clean and non-polluting sustainable energy has attracted extensive interest of researchers around the world. Hydrogen is an excellent energy carrier due to its advantages of high energy density and environmental friendliness. Photocatalytic water-splitting is a promising way to produce hydrogen. However, there is a long way to go for its large-scale application for hydrogen production because of the relatively low energy conversion efficiency of photocatalysis at present. Therefore, it is still a challenge to find a photocatalytic material with high utilization efficiency of sunlight and good stability [1–11].

Among many photocatalytic materials, metallic sulfides have been widely studied due to their narrow band gaps and high utilization of solar light. CdS with the band gap of 2.4 eV, as a typical semiconductor photocatalytic material, has good response to visible light and high conduction band position, which is favorable to reduce H^+ to hydrogen. Therefore, it has become a research hotspot [12–18]. However, CdS is easily oxidized by photogenerated holes, resulting in self-corrosion. Moreover, CdS has high photogenerated carrier recombination rate, which leads to its poor photocatalytic performance for hydrogen production [19–21]. Therefore, loading co-catalysts or combining other semiconductors to form heterostructures are effective ways to improve the photocatalytic activity and stability for hydrogen production [22–27]. It is well known that Pt and other precious metals are excellent co-catalysts for hydrogen evolution, but the high price and scarce resource make them unsuitable to be applied in a large scale [28–30]. Therefore, it is highly necessary to look for cheap and abundant non-precious metal catalysts to replace Pt and other precious metals as co-catalysts of CdS for photocatalytic hydrogen production [31–38].

Recently, non-noble metal sulfide has become a research hotspot of co-catalyst, such as Co_9S_8 , which is a very promising catalytic material for photocatalytic hydrogen production because of narrow band gap and high flat band potential [39–42]. CoS_x is widely used in electrocatalytic water decomposition and oxygen reduction with excellent electrochemical properties [43,44]. However, as far as we know, CoS_x has not been widely used in photocatalytic water-splitting. Qiu et al. [40] designed and synthesized a kind of direct Z-type semiconductor heterostructure photocatalytic material $\text{Co}_9\text{S}_8/\text{CdS}$ with hollow Co_9S_8 nano-cube supported CdS quantum dots. In this study, hollow cube $\text{Co}(\text{OH})_2$ was used as a template, and dimethyl sulfoxide (DMSO) was used as a solvent and S source to form Co_9S_8 by

ion exchange with OH^- . In visible light, compared with the pure hollow Co_9S_8 cube and CdS quantum dot, the hydrogen production yield of the $\text{Co}_9\text{S}_8/\text{CdS}$ catalyst was improved by 134 times and 9.1 times, respectively. In addition, the hydrogen production activity of the $\text{Co}_9\text{S}_8/\text{CdS}$ catalyst remained relatively stable for 25 h. However, this method required the use of toxic organic reagents and complex preparation processes. Reddy [45] designed and synthesized a Z-type photocatalyst composed of $\text{Co}-\text{C@Co}_9\text{S}_8$ double-shell nanocage supported mesoporous reticular CdS, which had a hydrogen production rate of $26.69 \text{ mmol g}^{-1} \text{ h}^{-1}$ and an apparent quantum yield of 7.82% at 425 nm for 5 h. Wang et al. synthesized a photocatalyst with layered $\text{Co}_9\text{S}_8/\text{ZnIn}_2\text{S}_4$ cage heterostructure [46], which effectively promoted the separation of photogenerated charges and exposed the redox active sites. The hydrogen production efficiency reached $6.25 \text{ mmol g}^{-1} \text{ h}^{-1}$ with good stability, but the disadvantage was that the powder sample was difficult to be recycled. Zheng et al. [41] designed and synthesized a CoS bifunctional catalyst with the hydrogen production rate of $1.197 \text{ mmol g}^{-1} \text{ h}^{-1}$, and the oxygen yield of up to 65%. Lin's research group [47] used Co_9S_8 for the first time to prepare a ternary $\text{TiO}_2/\text{Co}_9\text{S}_8/\text{POM}$ composite material as photoanode for photoelectrochemical (PEC) water oxidation, and the current density was as high as 1.12 mA cm^{-2} vs RHE at AM1.5. However, the preparation process of this material was too complicated.

Here, a simple method was designed to synthesize a composite catalyst by using CdS nanorod array (NRs) as skeleton, and then loading CoS_x nanosheet onto the CdS nanorod. According to the previous work of our research group [48], firstly, one-dimensional CdS NRs were grown on FTO, and then the intermediate containing Co was loaded onto the CdS NRs through simple chemical bath deposition (CBD) [49] in cobalt chloride and urea solution. Finally, CdS- CoS_x was obtained through simple ion exchange. The preparation process is simple and the prepared structured catalyst is easy to be recycled. The photocatalytic hydrogen evolution performance of CdS- CoS_x composite catalyst was significantly improved compared with that of single component catalyst CdS. The prepared composite catalyst was used as a photoanode for PEC hydrogen production, and its performance was comparable to that of CdS-Pt sample. So CoS_x can replace precious metal Pt, showing a promising application. In addition, in $\text{Na}_2\text{S}-\text{Na}_2\text{SO}_3$ system for PEC hydrogen production, we found that the measured photocurrent showed an opposite change rule with the hydrogen production yield. By designing a series of experiments, the reaction network for this photocatalytic system was analyzed for the first time, and the photocatalytic and photoelectrochemical hydrogen production process was explained reasonably.

Experimental

Catalysts preparation

One-dimensional CdS NRs were synthesized according to the hydrothermal methods reported previously by our group [48]. In a typical experiment, a clean $3 \times 5 \text{ cm}^2$ FTO with the conductive side facing down was immersed in Teflon-lined stainless steel autoclave (100 mL) containing 0.05 mol/L cadmium nitrate (99% Aladdin), 0.05 mol/L thiourea (99% Aladdin) and 0.01 mol/L glutathione (99% Aladdin), and then the autoclave was transferred to an oven and maintained at 210°C for 12 h. After that, the CdS NRs film on FTO was alternately rinsed with distilled water and alcohol for several times, dried naturally, then annealed at 450°C for 2 h under pure Ar.

The obtained CdS NRs film on FTO (conductive side facing down) was immersed in mixed solution containing 0.01 mol/L urea (99% Aladdin) and 0.015 mol/L cobalt chloride (99% Aladdin) under 90°C for 1 h, 2 h, 3 h, 4 h, respectively, to load the intermediate containing cobalt ($\text{Co}(\text{CO}_3)_{0.35}\text{Cl}_{0.20}(\text{OH})_{1.10}$, LCCH) [49] onto the CdS nanorods. After cooling down, the as-prepared samples were transferred to Teflon-lined stainless-steel autoclaves (100 mL) containing 5 mmol/L Na_2S solution. Then the autoclave was maintained at 90°C for 21 h. Finally, the sample was rinsed, dried, and the resultant sample was labeled as CdS- CoS_x -t, where “t” represented the chemical deposition time (1–4 h). The catalyst preparation process is illustrated in Scheme 1.

For comparison, CdS–Pt catalyst was prepared using the currently accepted photochemical reduction method. 300 μL 0.01 mol/L of H_2PtCl_6 and 300 μL of absolute ethanol were uniformly mixed, dropped on the CdS nanorods prepared above. The sample was then in situ photo-deposited under AM 1.5. The obtained sample was labeled as CdS–Pt.

Material structure and photoelectric chemical characterizations

The crystal phase composition of the photocatalysts were characterized by X-ray powder diffractometry (XRD, Bruker D8 Advance). The surface microstructure and elemental mappings of the photocatalysts were measured by field emission scanning electron microscope (SEM, ZEISS Merlin, In-lens, Germany), transmission electron microscopy (TEM, JEM-2100F, Japan) and energy dispersive X-ray detector (EDX, Bruker, XFlash 5030T, Germany). The surface chemistry state was analyzed by X-ray photoelectron spectroscopy (XPS, Kratos, Britain). The optical properties of the samples were

examined by ultraviolet–visible diffuse reflectance spectroscopy (DRS, U3010, Hitachi, Japan). The photoluminescence (PL) spectra of samples were tested by an F-7000 fluorescence spectrophotometer (Hitachi, Japan). The slit width of excitation and emission was 10 nm, the PMT voltage was 700 V, the excitation wavelength was 400 nm, and the scanning speed was 1200 nm min^{-1} . The Surface photovoltaic (SPV) of samples were tested by surface photovoltage test system (CEL-SPS1000). The element content samples were analyzed by inductively coupled plasma atomic emission spectrometer (ICP-OES, Agilent 720 ES).

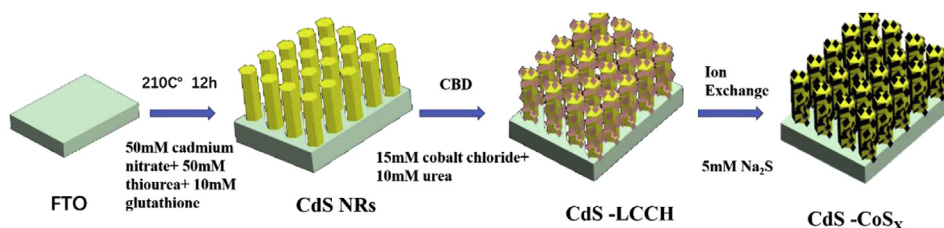
Photoelectrochemical performances of samples were performed using CHI660D electrochemical workstation with a three-electrode setup. Platinum net was used as the counter electrode, Ag/AgCl electrode was used as the reference electrode, and the as-prepared samples were served as the working electrode. The tests were conducted in electrolyte of 0.5 M Na_2S –0.5 M Na_2SO_3 mixed solution and light source was 300 W Xenon lamp with AM1.5 filter. Mott-Schottky plots acquired at 1000 Hz in 0.5 M Na_2S –0.5 M Na_2SO_3 mixed solution under dark condition.

Measurement of photocatalytic hydrogen production

The photocatalytic hydrogen evolution of the samples was carried out in a quartz closed photocatalytic hydrogen production system (CEL-SPH2N-D, Beijing). A piece of the structured catalyst (active area $3 \times 3 \text{ cm}^2$) was immersed in 150 ml of a mixed solution containing 0.5 M Na_2S –0.5 M Na_2SO_3 . The photocatalytic reaction was conducted under visible light irradiation (300 W Xe lamp with 420 nm cut-off filter) and vacuum environment of less than -0.09 Mpa and temperature of 5°C . Hydrogen was detected using GC-9790 gas chromatograph with molecular sieve 5 A packed column and thermal conductivity detector.

Measurement of photoelectrochemical hydrogen production

The photoelectrochemical reaction was implemented in CHI660D electrochemical workstation with three-electrode system. Platinum net was used as the counter electrode, Ag/AgCl electrode was used as the reference electrode, the as-prepared sample was served as the working electrode (effective area $1 \times 1.5 \text{ cm}^2$). The hydrogen is collected by drainage as shown in Fig. S1. In the reaction system, the sacrificial agent is the mixed solution of 0.5M Na_2S –0.5M Na_2SO_3 . The simulated solar light source is 300 W Xenon lamp with light intensity of 82 mW cm^{-2} , and the reaction temperature is room temperature (25°C).



Scheme 1 – Preparation process of CdS- CoS_x .

Results and discussion

Material structure characterizations

Fig. 1A shows that pure CdS is hexahedral prism structure, growing uprightly on FTO. Fig. 1(B–F) are SEM images of CdS NRs coated with CoS_x. It can be seen clearly that CoS_x nanosheets are uniformly distributed on the outer surface of CdS NRs, and the loading of CoS_x nanosheets gradually increases with the increase of deposition time. When the deposition time reaches 4 h, excess CoS_x completely covers the entire CdS NRs (Fig. 1F).

Fig. 2 shows TEM images of CdS-CoS_x-3 and CdS. As shown in Fig. 2A, CdS exhibits short rod shape, the average length and average width of CdS have been measured to be 775 nm and 340 nm respectively. Fig. 2B is the HRTEM image of CdS, where the lattice diffraction fringes of the CdS (002) crystal plane can be observed. From Fig. 2C, it can be seen clearly that CoS_x nanosheets are layered on the surface of CdS. But it is hard to observe any lattice fringes of CoS_x in Fig. 2D, indicating that CoS_x exists mainly in amorphous form. The surface element distribution mappings of CdS-CoS_x-3 are shown in Fig. 2(E–G), corresponding to Cd, S, and Co, respectively, indicating that CoS_x nanosheets are uniformly distributed on the surface of the CdS NRs. The TEM images of other CdS-CoS_x samples are shown in Fig. S2 (H–J).

The XPS spectra of CdS-CoS_x-3 are shown in Fig. 3. In Fig. 3A, the characteristic peaks at 411.73 eV and 404.98 eV correspond to 3d_{3/2} and 3d_{5/2} of Cd²⁺, respectively. In Fig. 3B, the characteristic peaks at 162.50 eV and 161.30 eV are attributed to 2p_{1/2} and 2p_{3/2} of S²⁻, respectively. The weak peak for elemental S can be found at around 168.3 eV. Fig. 3C can be fitted to three pairs of peaks. One pair of the satellite peaks of Co are located on 803.38 eV and 787.04 eV. The other pair of peaks at 798.75 eV and 783.29 eV are assigned to 2p_{1/2} and 2p_{3/2} of Co³⁺, and the third pair of peaks at 797.05 eV and 781.13 eV are ascribed to 2p_{1/2} and 2p_{3/2} of Co²⁺, respectively. According to the calculated peak areas, the content ratio of Co²⁺ to Co³⁺ is 1.76. Therefore, the prepared CoS_x is composed of Co²⁺ and Co³⁺, mainly Co²⁺. Compared with the XPS spectra of CdS as shown in Fig. S3, it can be found that the peak positions of Cd and S in CdS-CoS_x-3 have a little shift after

loading CoS_x, which is probably caused by the strong interaction between CdS and CoS_x. The XPS spectra for CdS-CoS_x-3 sample before and after cycling stability test are shown in Fig. S4. It is obvious that the chemical state of CdS-CoS_x-3 after stability test has hardly changed.

The XRD patterns of CdS-CoS_x, CdS and CoS_x powders are shown in Fig. 4A and Fig. S5. There is no significant difference between CdS and CdS-CoS_x, and all samples have diffraction peaks corresponding to CdS and FTO, but no diffraction peaks of CoS_x are found in CdS-CoS_x samples. The possible reason is that CoS_x mainly exists in amorphous form, or the load of CoS_x is too low. The XRD patterns of used CdS-CoS_x-3 and CoS_x powder are shown in Fig. S5. It is obvious that the physical structure of CdS-CoS_x-3 has hardly changed after stability test. The actual contents of Co, Cd, S elements in the CdS-CoS_x-3 and CdS measured by inductively coupled plasma optical emission spectrometer (ICP-OES) are shown in Table S2. It is known that the real Co content of the prepared samples with optimum performance is 2.1%. Fig. 4B shows that the absorption intensity of the samples in the visible and ultraviolet light region increases with the extension of deposition time. When the deposition time extends to 4 h, the absorbance of CdS-CoS_x-4 in the 300–500 nm region decreases, indicating that the excessive loading of CoS_x is not conducive to the absorption of visible light. The curves of (Ahν)² vs hν for all samples are shown in Fig. S6. It can be obtained that the band gap of CdS and CdS-CoS_x-3 is 2.25 eV and 2.32 eV, respectively. Fig. 4C shows that the fluorescence intensity of CdS-CoS_x is higher than that of CdS. This is because the carrier concentration of CdS-CoS_x increases significantly after loading CoS_x, leading to an increase in the amount of photo-generated carrier recombination. However, the fluorescence intensity of CdS-CoS_x-3 is the lowest among all CdS-CoS_x samples, indicating that proper CoS_x loading can reduce the recombination of photogenerated carriers.

Fig. 5A and B show the time-resolved photoluminescence (TRPL) patterns of CdS and CdS-CoS_x-3, respectively. TRPL spectra were fitted in polynomial $R(t) = A_1e^{(-t/\tau_1)} + A_2e^{(-t/\tau_2)}$. The fluorescent lifetime τ_1 and τ_2 were calculated to be 1.24 ns, 3.94 ns for CdS and 1.16 ns, 2.88 ns for CdS-CoS_x-3, respectively. It is obvious that the fluorescence lifetime of CdS-CoS_x-3 is slightly lower than that of CdS, which is possibly due to the

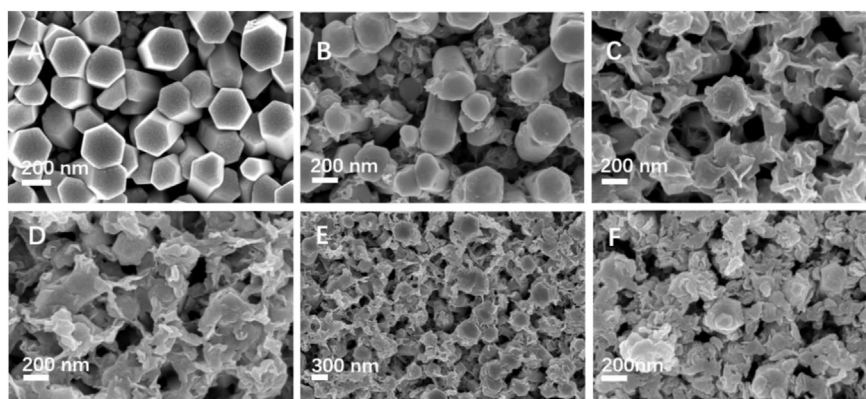


Fig. 1 – SEM images of (A) CdS, (B) CdS-CoS_x-1, (C) CdS-CoS_x-2, (D, E) CdS-CoS_x-3, (F) CdS-CoS_x-4.

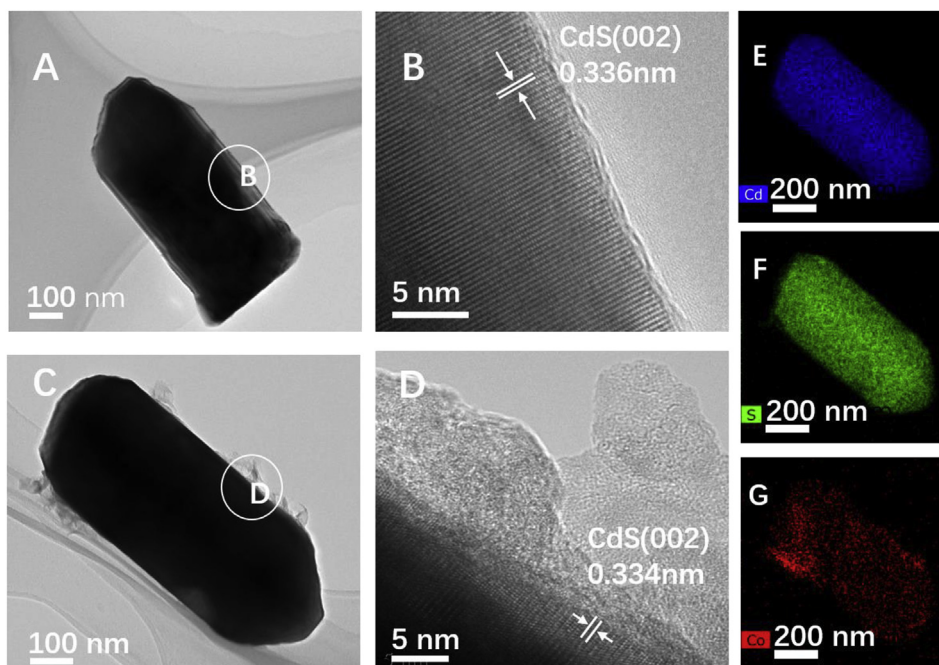


Fig. 2 – (A-B) TEM and HRTEM images of CdS. (C-D) TEM and HRTEM images of CdS-CoS_x-3. (E-G) EDX element mappings of CdS-CoS_x-3.

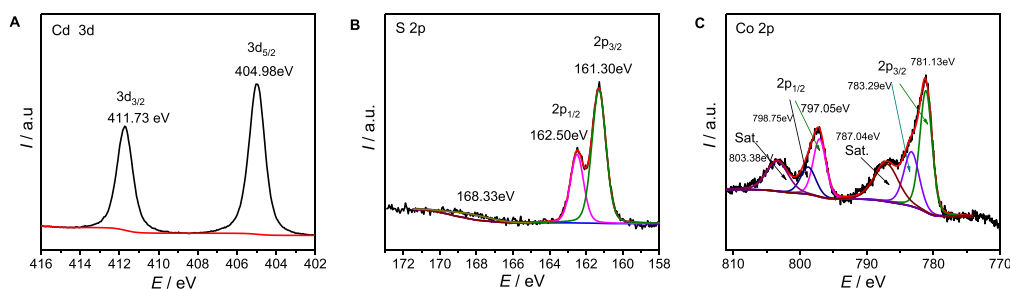


Fig. 3 – XPS spectra for (A) Cd 3d, (B) S 2p and (C) Co 2p of the CdS-CoS_x-3.

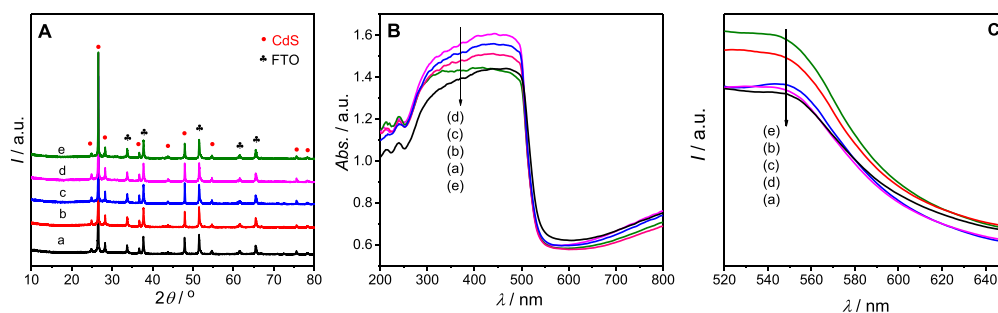


Fig. 4 – (A) XRD patterns, (B) UV-vis diffuse reflectance spectra and (C) photoluminescence patterns of (a) CdS, (b) CdS-CoS_x-1, (c) CdS-CoS_x-2, (d) CdS-CoS_x-3, (e) CdS-CoS_x-4.

increase of charge transfer rate of CdS after loading CoS_x. Fig. 5C exhibits the surface photovoltage (SPV) spectra of CdS and CdS-CoS_x-3. It can be seen that the SPV value of CdS is higher than that of CdS-CoS_x-3, indicating that less photo-generated electrons or more holes in CdS migrated to the

surface after loading CoS_x, and it is possibly because of the lower fermi level of CoS_x than that of CdS. As discussed above, we deem that an appropriate amount of CoS_x can effectively promote the transfer capability of photogenerated charge carrier in CdS.

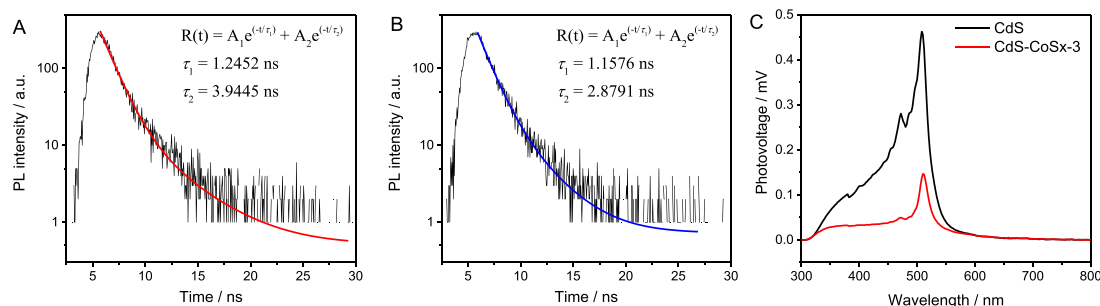


Fig. 5 – Time-resolved photoluminescence patterns of (A) CdS and (B) CdS-CoS_x-3 and (C) surface photovoltaic patterns under the condition of completely protection from light of CdS and CdS-CoS_x-3.

Photocatalytic and photoelectrochemical hydrogen production

In order to study the carrier concentration and photocatalytic properties of all the samples, the Mott-Schottky curves and photocatalytic H₂ production were tested. Fig. 6A shows the slopes of normalized Mott-Schottky plots. As exhibited in Table S1, the calculated carrier concentration increases along with the increase of deposition time, but when the deposition time increases to 4 h, the excessive loading of CoS_x reduces the carrier concentration. The calculated E_{CB} values of CdS and CdS-CoS_x-3 are shown in Fig. S7. Combined with Fig. S6, it can be deduced that E_{VB} values of CdS and CdS-CoS_x-3 are 3.33 eV and 3.35 eV, respectively. Under visible light irradiation, the hydrogen evolution rates of all samples are displayed in Fig. 6B. CdS without co-catalyst has almost no hydrogen produced by photocatalysis. After loading CoS_x, the hydrogen production rate of CdS-CoS_x increases rapidly, among which the hydrogen production rate of CdS-CoS_x-3 is the highest (3.5 $\mu\text{mol cm}^{-2} \text{h}^{-1}$). The cyclic stability of CdS-CoS_x-3 for photocatalytic hydrogen production is displayed in Fig. 6C, demonstrating that the photocatalytic stability of CdS-CoS_x-3 is very good after at least 5 cycles. However, the photocatalytic hydrogen production activity of CdS-CoS_x is about 1/4 of that of CdS-Pt, indicating that the activity of CoS_x as a co-catalyst is still lower than that of precious metal Pt (Fig. 6B-d and f).

The PEC hydrogen production was carried out with the schematic device shown in Fig. S1 and the results shown in Fig. 7A. It can be seen clearly from Fig. 7A that the PEC

hydrogen production rate of CdS-CoS_x samples is greatly improved compared with that of photocatalytic hydrogen production (Fig. 5B). The PEC hydrogen production rate of CdS-CoS_x-3 is 2.7 times that of CdS, reaching 168.6 $\mu\text{mol cm}^{-2} \text{h}^{-1}$ (37.77 L m⁻² h⁻¹), which is the same as that of CdS-Pt. The recycling stability of CdS-CoS_x-3 for PEC hydrogen production is shown in Fig. 7B. After 5 cycles, the hydrogen production rate of the sample was reduced to 74%, indicating that the sample was subjected to some degree of photo-corrosion during PEC hydrogen production.

The linear sweep voltammetric (LSV) curves of all samples under dark and AM1.5 illumination are shown in Fig. 8A. At the positive bias voltage, all samples have much higher current densities under light irradiation than those in the dark, owing to the transfer of photogenerated electrons from the sample to counter electrode (Pt net). After deposited Pt on CdS, the photocurrent of CdS-Pt was obviously lower than that of pure CdS, which is possibly because of the excellent electron capture ability of the loaded Pt [35]. Fig. 8B shows the time-passed photocurrent curves (i-t curve) of the as-prepared samples at the bias voltage of 1.0 V (vs. RHE). It is obvious that the photocurrent density of CdS-Pt exhibits the smallest among all the samples. As the loading time of CoS_x increases from 1 to 3 h, the photocurrent of CdS-CoS_x decreases gradually. We deem that it is also because of the electron capture ability of the loaded CoS_x as a reductive cocatalyst. While the loading time of CoS_x reaches to 4 h, the photocurrent density of CdS-CoS_x obviously increases. As shown in the SEM images (Fig. 1), the loaded CoS_x obviously agglomerates in the CoS_x-

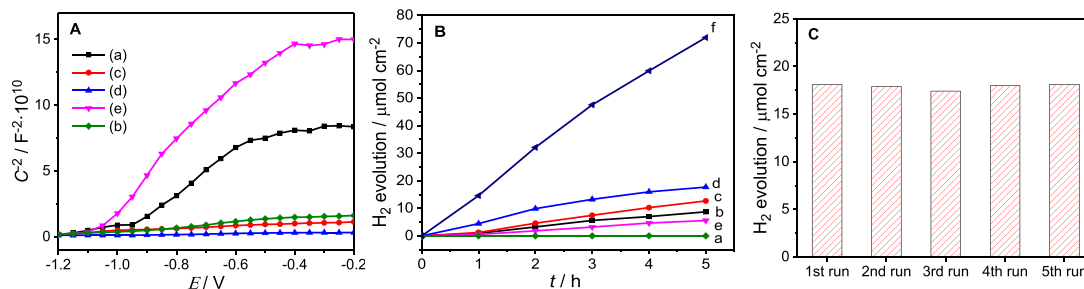


Fig. 6 – (A) Mott-Schottky plots acquired at 1000 Hz in 0.5 M Na₂S-0.5 M Na₂SO₃ mixed solution under dark condition. (B) The photocatalytic H₂ production in 0.5 M Na₂S-0.5 M Na₂SO₃ mixed solution under visible light irradiation on (a) CdS, (b) CdS-CoS_x-1, (c) CdS-CoS_x-2, (d) CdS-CoS_x-3, (e) CdS-CoS_x-4 and (f) CdS-Pt. (C) The recycling stability of CdS-CoS_x-3 under visible light irradiation for 5 h.

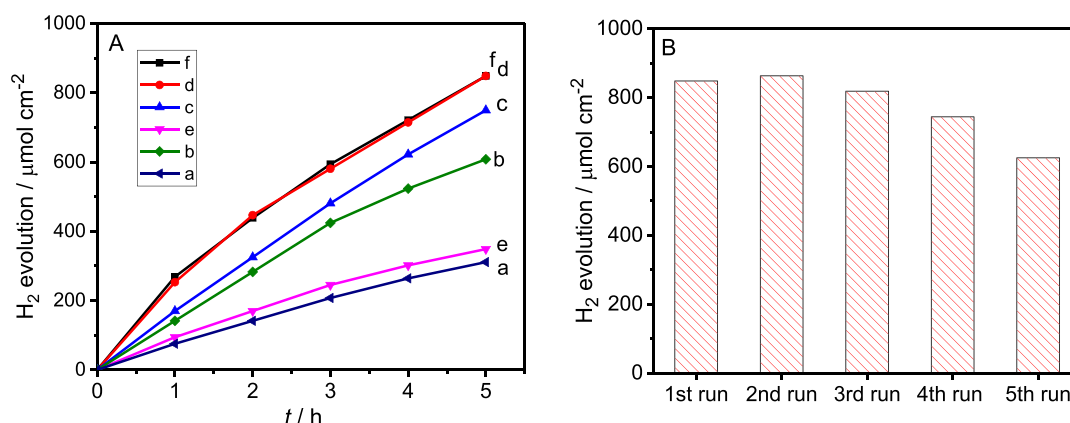


Fig. 7 – (A) The PEC hydrogen production at the potential of 0.6 V (vs. RHE) in 0.5 M Na₂S-0.5 M Na₂SO₃ solution under 300 W Xe lamp irradiation on (a) CdS, (b) CdS-CoS_x-1, (c) CdS-CoS_x-2, (d) CdS-CoS_x-3, (e) CdS-CoS_x-4, (f) CdS-Pt. (B) The recycling stability of CdS-CoS_x-3 at the potential of 0.6 V (vs. RHE).

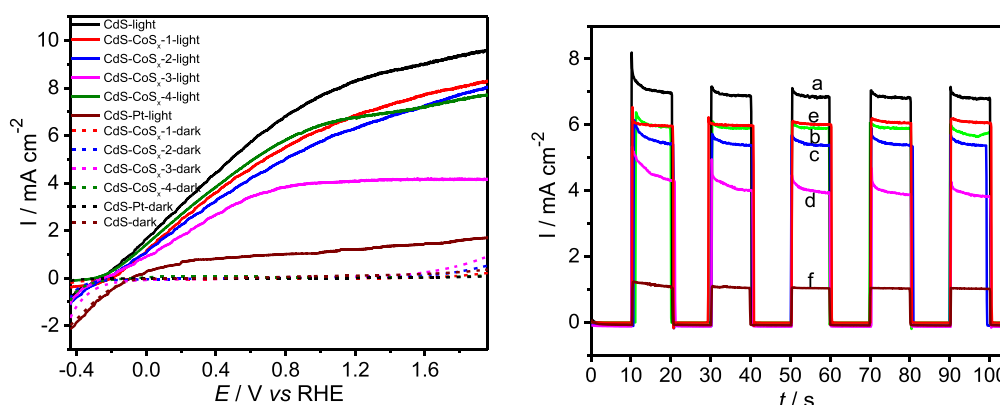


Fig. 8 – The polarization curves of samples (A), photocurrent density profiles under AM1.5 irradiation at the bias potential of 1.0 V (vs. RHE) (B) on (a) CdS, (b) CdS-CoS_x-1, (c) CdS-CoS_x-2, (d) CdS-CoS_x-3, (e) CdS-CoS_x-4 and (f) CdS-Pt.

CdS-4 sample. It is reported that the bulk CoS_x shows the properties of semiconductor [40]. According to the band structure of CoS_x and CdS, the electrons on the CB of CoS_x might transfer to the CB of CdS, hence increases the photocurrent density of CdS-CoS_x.

The reaction network analysis for photocatalytic hydrogen production

In the general PEC hydrogen production process, the photoelectrons of the working electrode are transferred to the counter electrode Pt by the external circuit to generate hydrogen. Therefore, the larger photocurrent corresponds to the higher photoelectrochemical hydrogen production rate. However, in this study, it is very interesting that the smaller photocurrent resulted in the higher photoelectrochemical hydrogen production rate. In fact, this phenomenon has also been found in TiO₂/MoS₂ system [50].

In order to explain this abnormal result, a series of experiments (Fig. S8) were designed to explore the reaction process and the results were shown in Fig. 9. From Fig. 9A, it can be seen that in 0.5 M Na₂S-0.5 M Na₂SO₃ solution (Fig. S8A), Pt

alone produces little hydrogen. While CdS-CoS_x-3 can produce hydrogen with the average hydrogen production rate of 44 μmol cm⁻² h⁻¹ for 5 h. It should be noted that the photocatalytic hydrogen production rate of CdS-CoS_x-3 in Fig. 9 is much higher than that in Fig. 5 because of different reaction temperatures and light sources. When Pt and CdS-CoS_x-3 were simultaneously inserted into 0.5 M Na₂S-0.5 M Na₂SO₃ solution (Pt and CdS-CoS_x-3 were not connected, Fig. S8B), the hydrogen production rate reaches 70 μmol cm⁻² h⁻¹, with 60% increase based on CdS-CoS_x-3. For CdS alone, the average hydrogen production rate is 8 μmol cm⁻² h⁻¹ for 5 h. However, the hydrogen production rate does not increase significantly when the Pt was inserted into solution. The hydrogen production performance of all samples was tested in the same case of Pt (Fig. S8B), and their hydrogen production rates are shown in Fig. S9. From these figures, all the photocatalysts exhibit enhanced hydrogen production rates when Pt is inserted simultaneously into the solution even if the Pt is not connected with the photocatalysts.

To this interesting phenomenon, we deduced the reason is that Na₂S₂O₃ would be formed during the photocatalytic reaction in Na₂S-Na₂SO₃ solution, then Na₂S₂O₃ reacts with

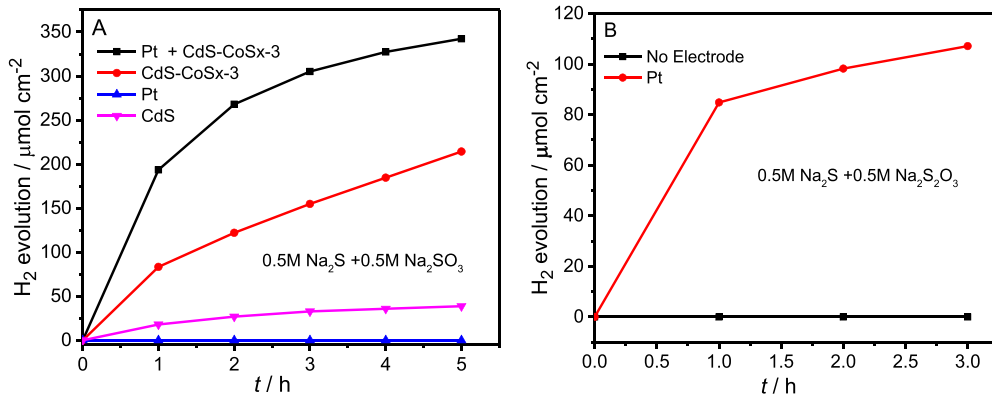


Fig. 9 – The photocatalytic H₂ production rates in 0.5M Na₂S-0.5M Na₂SO₃ (A) and 0.5M Na₂S-0.5M Na₂S₂O₃ (B) solution under 300 W Xe lamp irradiation at different experimental situations (see Fig. S8).

water to release H₂ on the Pt electrode, thus increasing the hydrogen production rate. In order to verify our conjecture, Pt alone was inserted in 0.5M Na₂S-0.5M Na₂S₂O₃ solution under irradiation for 3 h, as shown in Fig. S8A, large amounts of hydrogen were observed in this system. However, H₂ was not produced in the 0.5M Na₂S-0.5M Na₂S₂O₃ solution under illumination without Pt, as shown in Fig. 9B. Therefore, it is preliminarily confirmed that Na₂S₂O₃ reacts with water to release H₂ on Pt electrode.

In order to further verify the formation of Na₂S₂O₃, we designed another experiment, as shown in Fig. S10. Firstly, a piece of CdS-CoS_x-3 alone was placed in 0.5M Na₂S-0.5M Na₂SO₃ solution under irradiation for 3 h, and then CdS-CoS_x-3 was taken out. Finally, Pt was put into the above solution and irradiated for 1 h. As expected, 1.2 mL hydrogen was produced, further indicating that the intermediate Na₂S₂O₃ is formed in 0.5 M Na₂S-0.5 M Na₂SO₃ system. Na₂S₂O₃ cannot be completely consumed in time on the CdS-CoS_x catalyst to generate hydrogen, while, Pt can enhance the redox reaction of Na₂S₂O₃ with water to release H₂. Therefore, when Pt and CdS-CoS_x are both present in Na₂S-Na₂SO₃ solution, the hydrogen production rate can be greatly improved.

Base on the above discussion, the photocatalytic reaction network in this catalytic system is proposed as follows (Eqs. (1)–(6)).

Photocatalytic reduction reaction :



$$E^0 = -0.828 \text{ V}; E = 0 \text{ vs RHE}$$

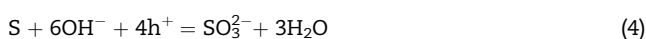


$$E^0 = -0.571 \text{ V [51]}; E = 0.257 \text{ vs RHE}$$

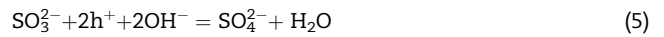
Photocatalytic oxidation reaction:



$$E^0 = -0.476 \text{ V [51]}; E = 0.354 \text{ vs RHE}$$

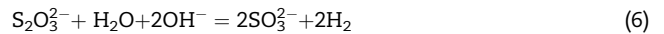


$$E^0 = -0.449 \text{ V [51]}; E = 0.369 \text{ vs RHE}$$



$$E^0 = -0.930 \text{ V [51]}; E = -0.102 \text{ vs RHE}$$

Photochemical redox reaction (on Pt surface):



In photocatalytic process, photogenerated electrons on CdS are transferred to CoS_x to undergo a series of photocatalytic reduction reactions (Eqs. 1 and 2), and the holes left on CdS undergo photocatalytic oxidation reactions (Eqs. (3)–(5)), facilitating electron-hole separation and producing an intermediate species Na₂S₂O₃. All reduction or oxidation potentials E^0 in equations (1)–(5) represent the standard potentials in 1 M NaOH. These potentials were referenced to the reversible hydrogen electrode (RHE). In 0.5 M Na₂S-0.5 M Na₂SO₃ solution (pH = 13.6, close to the standard alkaline environment of 14), these reactions can occur theoretically on CdS-CoS_x catalyst as shown in Fig. 10. According to the redox potentials, the reduction of Na₂SO₃ into Na₂S₂O₃ is easier than H₂O into H₂. Furthermore, the aforementioned experimental results (Fig. 9B and Fig. S10) have verified that the intermediate Na₂S₂O₃ can occur photochemical redox reaction on Pt to release H₂ (Eq. (6)). Therefore, when Pt and CdS-CoS_x are both present in system, the produced Na₂S₂O₃ by photocatalysis on CdS-CoS_x can diffuse to the Pt surface to generate H₂, thus enhancing hydrogen production even though two electrodes are not connected (it can be understood that the external circuit photocurrent is 0).

Based on the reaction network analysis, it is easy to understand the abnormal phenomenon in PEC hydrogen production process, that is, low photocurrent leads to high hydrogen production rate. In PEC system, the external bias can promote the separation of the photogenerated electron-hole, and the photoelectrons flow into counter electrode Pt (photocurrent) to reduce water to H₂. Although pure CdS yield few H₂ in photocatalysis process due to recombination of electron-hole (Fig. 6B-a), the photogenerated electrons can reduce H⁺ to H₂ on the Pt electrode when bias potential is

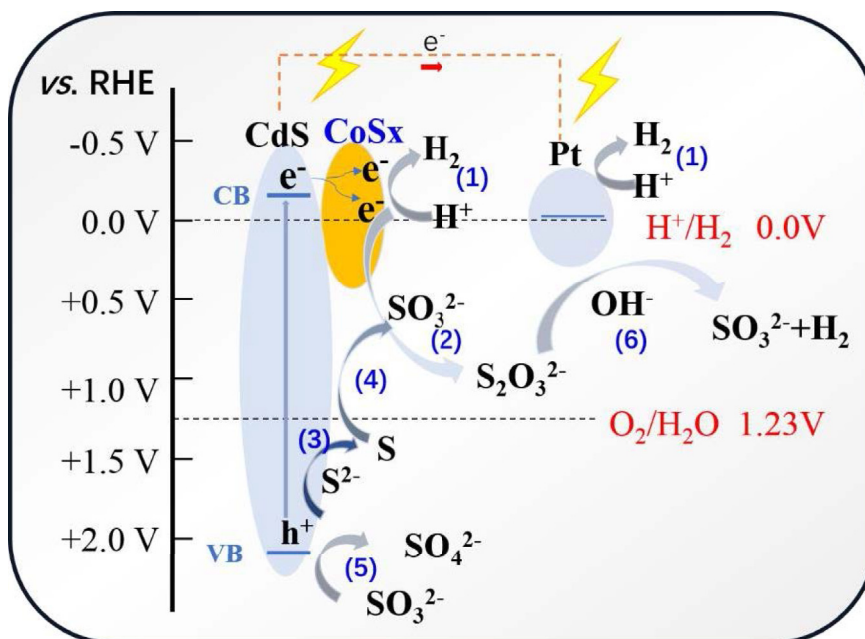


Fig. 10 – Reaction network of photocatalytic hydrogen production in Na_2S – Na_2SO_3 system.

applied, resulting in increased PEC hydrogen production (Fig. 7A-a). For the CdS– CoS_x system, the photogenerated electrons on CdS are further separated under external bias and transferred to the co-catalyst CoS_x firstly. The photocatalytic reduction reactions (Eqs. 1 and 2) tend to occur on CoS_x , and most photoelectrons are involved in these reactions, rather than flowing to the counter electrode through the external circuit, thus a decreased photocurrent. The easier the photocatalytic reaction (Eq. (2)) is, the smaller the photocurrent measured by the external circuit is, and the more $\text{S}_2\text{O}_3^{2-}$ is generated, resulting in more H_2 is generated on Pt electrode. Moreover, the rest of the photogenerated electrons also flows to the counter electrode (photocurrent) to participate in water reduction. It can be concluded that the stronger catalytic activity of CdS– CoS_x is, the smaller photocurrent is and the higher hydrogen production efficiency is.

Through the above analysis, it is easy to explain that the photocatalytic hydrogen production activity of CdS– CoS_x (without Pt) is much lower than that of CdS–Pt (Fig. 6B-d and f). However, the PEC hydrogen production rate on CdS– CoS_x is obviously improved due to the synergistic effect with the Pt electrode and CdS– CoS_x . In particular, the CdS– CoS_x -3 catalyst has the same PEC hydrogen production efficiency as CdS–Pt (Fig. 7B-d and f), indicating the potential of CoS_x replacing precious metal Pt in PEC hydrogen production.

Conclusions

A novel structural catalyst CdS– CoS_x has been synthesized by a simple method, in which CoS_x acts as co-catalyst to accept photoexcited electrons of CdS, thereby improving the hydrogen production activity and stability of CdS. Under the simulated solar light, the PEC hydrogen production rate using

CdS– CoS_x as photoanode reaches $168.6 \mu\text{mol cm}^{-2} \text{h}^{-1}$ ($37.77 \text{ L m}^{-2} \text{h}^{-1}$), which is 2.7 times that of CdS and the same as that of CdS–Pt. The prepared CdS– CoS_x is easy to recycle, and CoS_x shows the potential of replacing precious metal Pt. More important, in this work, an abnormal relationship between photocurrent and hydrogen production was found in the Na_2S – Na_2SO_3 system for PEC hydrogen production. A series of experiments were reasonably designed to explain this abnormal phenomenon and reveal the photocatalytic and PEC hydrogen production characteristics. The reaction network in Na_2S – Na_2SO_3 system for photocatalytic hydrogen production has been proposed and verified for the first time. It can be concluded that the stronger catalytic activity of CdS– CoS_x is, the smaller photocurrent is and the higher hydrogen production efficiency is.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2019.09.078>.

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