Redox Dual-Cocatalyst-Modified CdS Double-Heterojunction Photocatalysts for Efficient Hydrogen Production

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ABSTRACT: Cadmium sulfide (CdS) as one of the most common visible-light-responsive photocatalysts has been widely investigated for hydrogen generation. However, its low solar−hydrogen conversion efficiency caused by fast carrier recombination and poor catalytic activity hinders its practical applications. To address this issue, we develop a novel and highly efficient nickel−cobalt phosphide and phosphate cocatalyst-modified CdS (NiCoP/CdS/NiCoPi) photocatalyst for hydrogen evolution. The dual-cocatalysts were simultaneously deposited on CdS during one phosphating step by using sodium hypophosphate as the phosphorus source. After the loading of the dual-cocatalysts, the photocurrent of CdS during one phosphating step by using sodium hypophosphate as the phosphorus source. After the loading of the dual-cocatalysts, the photocurrent of CdS significantly increased, while its electrical impedance and photoluminescence emission dramatically decreased, which indicates the enhancement of charge carrier separation. It was proposed that the NiCoP cocatalyst accepts electrons and promotes hydrogen evolution, while the NiCoPi cocatalyst donates electrons and accelerates the oxidation of sacrificial agents (e.g., lactic acid). Consequently, the visible-light-driven hydrogen evolution of this composite photocatalyst greatly improved. The dual-cocatalyst-modified CdS with a loading content of 5 mol % showed a high hydrogen evolution rate of 80.8 mmol·g−1·h−1, which was 202 times higher than that of bare CdS (0.4 mmol·g−1·h−1). This is the highest enhancement factor for metal phosphate-modified CdS photocatalysts. It also exhibited remarkable stability in a continuous photocatalytic test with a total reaction time of 24 h.

KEYWORDS: cadmium sulfide, phosphate, phosphorus, double heterojunctions, photocatalytic hydrogen evolution

1. INTRODUCTION

Using semiconductor materials to directly convert solar energy into hydrogen energy is regarded as a promising approach to the storage of renewable energy.1−3 The practical application of this technology requires the design and development of low-cost and highly active photocatalysts, which usually consist of a semiconductor as a solar light absorber and a noble metal (e.g., gold, platinum, or palladium) as a hydrogen evolution cocatalyst.4−6 During the photocatalytic process, the semiconductor harvests and converts solar light and generates electron−hole pairs (i.e., charge carriers) that can be spatially separated by the in-built electric field at the metal−semiconductor heterojunction.7 The electrons migrating to the noble metal cocatalyst are eventually captured by the protons adsorbed on its surface, while the holes remaining in the semiconductor oxidize sacrificial reagents in the aqueous solution. Regarding the selection of semiconductor photocatalysts, cadmium sulfide (CdS) is considered as a model candidate because of its desirable bandgap \( E_g \approx 2.4 \text{ eV} \) for visible-light-driven photocatalysis and appropriate band-edge potentials for water splitting.7,8 However, like other semiconductors, pure CdS suffers from extremely low solar-hydrogen conversion efficiency, because of its low charge-separation efficiency and poor catalytic activity toward water reduction.9 As to the choice of hydrogen evolution cocatalysts, earth-abundant transition metal compounds, such as metal oxides,10−12 metal sulfides,13−16 metal carbides,17−19 metal nitrides,20−22 and metal phosphides (MP),23−29 that have relatively high mechanical strength, electrical conductivity, and chemical stability, have been explored as promising alternatives to noble-metal cocatalysts.

Metal phosphorus compounds, including MP and metal phosphates (MPs), have been widely used as hydrogen evolution reaction (HER) cocatalysts.23,24 Recently, transition MPs with a large number of unsaturated coordination surface atoms have attracted particular attention in photocatalytic hydrogen evolution.25−27 Liu and Rodriguez theoretically predicted that nickel phosphide (Ni1P) might be the best practical cocatalyst for hydrogen evolution.28 So far, many MPs, such as Ni1P,28 CoP,23,24 FeP,25,26 Cu1P,27 and MoP,29 have been fabricated and coupled with CdS as hydrogen production.
evolution cocatalysts. Their photocatalytic activity was typically 4–67 times higher than that of bare CdS (see more comparison details in Table S1). Further improvement of photocatalytic activity requires the codeposition of an oxidation cocatalyst that facilitates the hole scavenging. Metal phosphates (MPI), which have open-framework structures with large channels and cavities, have been proved to be good water oxidation catalysts in the electrocatalytic oxygen evolution reaction. Therefore, metal phosphates (MPI) can be used as oxidation cocatalysts in photocatalysis.

It has recently been demonstrated that a double-heterojunction photocatalytic system containing both reduction and oxidation cocatalysts exhibited better photocatalytic hydrogen evolution performance than their single-cocatalyst counterparts. For example, Yang et al. reported a dual-cocatalyst Pt/CdS/PdS system with Pt and PdS as reduction and oxidation cocatalysts, respectively, which showed activity 1.76 times higher than that of Pt/CdS. More recently, Wei et al. developed a new dual-cocatalyst system by replacing precious metal-containing redox cocatalysts with low-cost carbon dots and NiS, which exhibited 5.4 time activity enhancement, compared with pristine CdS.

Despite some impressive progress in the development of dual-cocatalyst containing photocatalysts, a general drawback of the existing systems is that they require a stepwise loading for dual-cocatalyst modification and often suffer from a low catalytic activity enhancement. To address these issues, we explore a new synthetic route that can simultaneously generate oxidation and reduction cocatalysts in a one-step phosphating reaction and achieve a highly efficient dual-cocatalyst-modified CdS photocatalyst, NiCoP/CdS/NiCoPi. The NiCoP-NiCoPi dual cocatalysts were deposited on CdS nanorods via a bimetal nickel–cobalt hydroxide precursor reacting with the volatile decomposition products from sodium hypophosphate at 300 °C and at a low flow rate of the inert carrier gas. The obtained NiCoP/CdS/NiCoPi double heterojunctions were characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) spectroscopy. The visible-light-driven hydrogen production by NiCoP/CdS/NiCoPi was tested and compared with CdS and Pt/CdS as references. The optimal loading content of the cocatalysts was found to be 5 mol %. The resulting photocatalyst showed a hydrogen evolution rate of 80.8 mmol·g⁻¹·h⁻¹ under visible light irradiation (>420 nm), 202 times and 17 times higher than those of pristine CdS (0.4 mmol·g⁻¹·h⁻¹) and Pt/CdS (7.6 mmol·g⁻¹·h⁻¹), respectively.

2. EXPERIMENT

2.1. Materials and Chemicals. All chemicals were of analytical grade, obtained from commercial suppliers and used without further purification. Cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O), urea (H₂NCONH₂), ethylenediamine (C₂H₄N₂), ammonium fluoride (NH₄F), and thiourea (NH₂CSNH₂) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Lactic acid, cadmium chloride hemipentahydrate (CdCl₂·2.5H₂O), and sodium hypophosphate (NaH₂PO₂) were purchased from Aladdin.

2.2. Catalyst Preparation. 2.2.1. Preparation of CdS Photocatalysts. CdS was prepared via a reported method. In a typical procedure, cadmium chloride hemipentahydrate and thiourea (molar ratio = 1:3) were put into 60 mL of ethylenediamine with continuous stirring for 30 min. Having been completely dissolved, the mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave and treated at 160 °C for 48 h. After cooling, the resulting yellow product was washed with distilled water and ethanol, and collected via centrifugation at 5000 rpm (Shanghai Anting, TDL-S-A). Then, the powder was dried at room temperature.

2.2.2. Preparation of NiCoP/CdS/NiCoPi Photocatalysts. 500 mg of as-synthesized CdS was added to 60 mL of deionized water containing cobalt(II) nitrate hexahydrate, nickel(II) nitrate hexahydrate, urea, and NH₄F with a molar ratio of 1:1:10:5. Then, the mixed solution was treated in a 100 mL Teflon-lined stainless steel autoclave at 120 °C for 10 h. The product was collected via centrifugation, washed by distilled water, and dried in vacuum at 60 °C to obtain the CdS/NiCo(OH)ₓ precursor. Finally, the obtained CdS/NiCo(OH)ₓ and an appropriate amount of NaH₂PO₂ (molar ratio = 1:10) were separately placed in two porcelain boats with NaH₂PO₂ upstream in the furnace, and treated at 300 °C for 2 h under 10 mL·min⁻¹ nitrogen flow. By adjusting the amount of nickel–cobalt precursor, NiCoP/CdS/NiCoPi photocatalysts with a NiCoP–NiCoPi theoretical loading contents of 1, 3, 5, 7, and 9 mol % were prepared. For comparison, two reference samples (i.e., NiCoP/CdS and NiCoP/CdS) were prepared via the reported methods. The NiCoP/CdS photocatalyst was prepared by changing the flow rate of carrier gas to 40 mL·min⁻¹. Meanwhile, the NiCoP/CdS photocatalyst was fabricated via slight modification of the method reported by Shi and Shen. Specifically, 500 mg of the obtained CdS/NiCo(OH)ₓ and 300 mg of NaH₂PO₂ were separately placed in two porcelain boats with NaH₂PO₂ upstream in the furnace, and treated at 150 °C for 2 h under 10 mL·min⁻¹ nitrogen stream.

2.3. Catalyst Characterization. Powder X-ray diffraction (XRD) patterns of the as-prepared photocatalysts were recorded with a Bruker D8 ADVANCE X-ray diffractometer using Cu Kα radiation. The morphology and microstructure were studied using a high-resolution transmission electron microscope (Tecnai model G2 F20 S-TWIN). Meanwhile, an energy-dispersive spectroscope attached to the TEM instrument was applied to perform elemental mapping of the catalysts. XPS analysis was performed on a VG ESCALAB 250 spectrometer using a monochromatic Al Kα X-ray. FTIR spectroscopy was analyzed with a FTIR spectrometer (Nicolet IS50, Thermo Fisher Scientific). The optical absorption of the samples was measured by a UV–vis diffuse reflectance spectrophotometer (Cary 500, Varian Co.) using BaSO₄ as a reflectance. Photoluminescence (PL) was examined with a FL/FS 920 TCSPC fluorescence spectrophotometer at an excitation wavelength of 420 nm.

2.4. Photoelectrochemical (PEC) Measurements. PEC measurements were performed on a CHI1030B electrochemical workstation using a conventional three-electrode cell with a Ag/AgCl reference electrode, a Pt counter electrode, and a prepared working electrode. To fabricate working electrodes, 10 μL of 10 mg·mL⁻¹ photocatalyst slurry (in dimethylformamide) was dropped onto a FTO substrate and then dried in air. Photocurrents were measured in the Na₂SO₄ (0.5 M) electrolyte solution using a 300 W xenon lamp with a band-cutoff filter (420 nm) as the light source. Electrochemical impedance spectroscopy (EIS) was measured over a frequency range from 0.01 to 10⁵ at an applied potential of 0.5 V using 10 mM K₃[Fe(CN)₆]₁/K₄[Fe(CN)₆] aqueous solution as the electrolyte.
2.5. Photocatalytic Hydrogen Evolution. Photocatalytic hydrogen evolution was carried out in a Pyrex cell in a top irradiation mode, and the cell was connected to a closed gas circulation and evacuation system (Perfectlight, Beijing, China). In a typical process, the catalyst (5 mg) was dispersed in 100 mL of the aqueous solution containing 10 vol % lactic acid as the sacrificial reagent with continuous stirring. Before the reaction, the system was sealed and vacuumed for 30 min. Then, the system was irradiated with a 300 W xenon lamp equipped with a band-cutoff filter (420 nm). The amount of evolved hydrogen was monitored using an in situ gas chromatograph (FULL, GC9790, TCD detector, China) with a thermal conductivity detector. Apparent quantum efficiency (AQE) was measured under different wavelength irradiation using band-pass filters (Pyrex, 420–600 nm), and calculated using follow equations (eq 1)

$$AQE(\%) = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\%$$

$$= \frac{\text{number of evolved H}_2 \text{molecules} \times 2}{\text{number of incident photons}} \times 100\% \quad (1)$$

3. RESULTS AND DISCUSSION

It has previously been reported that sodium hypophosphite can decompose into low valence state products (e.g., phosphine and phosphorus) and high valence state products (e.g., pyrophosphates, phosphates, and metaphosphates) at an elevated temperature of ≥150 °C via disproportionation reactions. The thermal decomposition products readily react with transition metal oxides or hydroxides, forming MP and MPi. Shi et al. showed that pure MP only formed in a reaction temperature range of 150–200 °C and/or at a high molar ratio (≥3) of hypophosphate to metal precursor. However, at a higher temperature (≥250 °C) or a lower [hypophosphate]/[metal precursor] ratio, a mixture of MP and MPi was obtained. The higher the reaction temperature was, the more MPi was obtained. Recently, we applied this method to the synthesis of NiCoP-decorated CdS photocatalysts, the flow rate of the inert carrier gas had a key impact on the final products, and only NiCoPi was obtained at 300 °C with a nitrogen flow rate of 40 mL·min⁻¹. It is generally accepted that sodium hypophosphite initially decomposes into phosphine (gas) and disodium hydrogen phosphate (melting point: ~250 °C) at 300 °C in an inert atmosphere through the following reaction

$$2 \text{NaH}_2\text{PO}_2 \xrightarrow{\Delta} \text{Na}_2\text{HPO}_4 + \text{PH}_3 \uparrow \quad (\text{eqn.2})$$

disodium hydrogen phosphate vapor (whose mobility is much slower than that of phosphine gas) reacts with the metal oxide or hydroxide precursors, forming MPi. It is easy for disodium hydrogen phosphate to evaporate at a temperature higher than its melting point. This also explains the observation of MP only at a low reaction temperature (150–200 °C) and MPi at a high reaction temperature (≥250 °C). That is to say, by tuning the reaction temperature and the flow rate of carrier gas, simultaneous formation of MP and MPi is feasible. Here, we carried out thermogravimetry (TG) and differential scanning calorimetry (DSC) for sodium hypophosphite, and summarized the decomposition of sodium phosphate at different temperatures and flow rates of carrier gas, as shown in Figures S1 and S2 in Supporting Information. MP as an excellent hydrogen evolution electrolyte catalyst for water reduction has received much attention in photocatalytic hydrogen production.33–35 Many reports have claimed successful syntheses of MP-modified CdS for hydrogen evolution. Yet, none or only a trace amount of MP was detected in the XPS analyses. Furthermore, MPi as an excellent water oxidation catalyst has also been widely investigated for water electrolysis.34–39 However, the role of the dominant MPi product in the previous MP/CdS systems was completely overlooked in photocatalytic hydrogen evolution.34

Herein, we demonstrate a dual-cocatalyst-modified CdS photocatalyst for hydrogen production, in which NiCoP and NiCoPi acted as reduction and oxidation cocatalysts, respectively. The fabrication of the photocatalyst is illustrated in Scheme 1. First, NiCo(OH)₃ was deposited on CdS via a hydrothermal reaction. Then, the precursor was phosphated using sodium hypophosphate as the phosphorus source at 300 °C under an inert atmosphere. It was found that the flow rate of inert gas should be low enough (≤10 mL·min⁻¹) to allow the metal hydroxide precursor to react with both phosphine and disodium hydrogen phosphate vapors, generating both NiCoP and NiCoPi cocatalysts on CdS. For a given cocatalyst loading concentration, the ratio between NiCoP and NiCoPi can be finely tuned by adjusting the [hypophosphate]/[metal precursor] ratio, which is discussed later.

The crystal structure of the as-prepared NiCoP/CdS/NiCoPi photocatalysts with varied loading amounts of NiCoP–NiCoPi cocatalysts from 1 to 9 mol % was analyzed by XRD. As shown in Figure 1a, all the diffraction peaks of bare CdS are consistent with the hexagonal structure of CdS (JCPDS card no. 41-1049). However, after the modification with NiCoP–NiCoPi cocatalysts, no obvious phase change in CdS is observed and no additional peaks from other phases appear. For 5% NiCoP/NiCoPi/CdS, inductive coupled plasma emission spectrometry (ICP-ES) (Table S2 in Supporting Information) confirmed that the actual loading...
content of co-catalysts was 3.52 mol %, being about 30% lower than the theoretical value (Table S3 in Supporting Information). Even when the theoretical loading is as high as 9 mol %, no other phase is observed in XRD patterns, indicating that the loaded materials might either be amorphous, or be too few and too small, which is verified by TEM analysis.

Infrared spectroscopy confirmed the existence of phosphates in NiCoP/Cds/NiCoPi. Figure 1b shows the FTIR spectra of bare CdS and 5 mol % NiCoP/Cds/NiCoPi samples. Compared with the bare CdS sample, 5 mol % NiCoP/Cds/NiCoPi photocatalyst shows extra FTIR absorption in the range of 500–1500 cm⁻¹. Specifically, the peaks at 1050 and 907 cm⁻¹ are assigned to the P=O stretching vibration. The broad absorption in the range of 700–800 cm⁻¹ is attributed to the P=S stretching vibrations. The peak at 570 cm⁻¹ is characteristic of the P-O bending vibrations. All of these indicate the successful loading of phosphates on CdS in NiCoP/Cds/NiCoPi.

The morphology and microstructure of the as-prepared bare CdS and 5 mol % NiCoP/Cds/NiCoPi photocatalysts were characterized by TEM. As shown in Figure 2a, the pristine CdS nanorods prepared in the first step (Scheme 1) have smooth surfaces with diameters of 30–100 nm. The HRTEM image of a CdS nanorod further shows its lattice structure and single crystalline nature (Figure 2b). It can be clearly seen that there are uniform lattice fringes with an interplanar spacing of 0.338 nm, which can be attributed to the (002) plane of CdS. 48 This result indicates that the nanorods grew along the direction of [001]. The fast Fourier transform (FFT) from the square (the inset in Figure 2b) reveals a structure of hexagonal CdS along the [010] zone axis. Upon the loading of NiCoP–NiCoPi cocatalysts, the nanorod morphology of CdS had no significant change, but the surface of nanorods became rough (Figure 2c).

The FFT pattern obtained from the square area (the inset in Figure 2d) is indexed to the (001), (111), and (110) planes of hexagonal NiCoP along the [110] zone axis (JCPDS card no. 71-2336), revealing the existence of crystalline NiCoP nanoparticles. 49 Elemental mapping (Figure 2f–k) shows that Ni, Co, P, and O are distributed over the whole surface of the CdS nanorod. The matching of the elemental distribution with the dark-field TEM image (the inset in Figure 2e) indicates a good dispersion of the dual-cocatalysts on CdS. In addition to TEM, we also studied the morphology and microstructure of CdS and NiCoP/Cds/NiCoPi with SEM. As shown in Figure S3, we did observe some surface roughness (as indicated with white circle marks) in NiCoP/Cds/NiCoPi, compared to CdS. However, no nanoparticles could be clearly observed on the surface of CdS upon the loading of NiCoP–NiCoPi cocatalysts. This may be because the loading amount was too low, and/or loaded cocatalysts were too small to be observed with SEM.

The chemical composition and surface electronic states of the as-prepared bare CdS and 5 mol % NiCoP/Cds/NiCoPi photocatalysts were characterized using XPS. The corresponding XPS spectra calibrated using C 1s (284.8 eV) as a reference are shown in Figure 3. Both pristine CdS and NiCoP/Cds/NiCoPi samples show two C 1s peaks of physically adsorbed carbon species (284.8 and 286.5 eV) (see Figure S4). The NiCoPi samples show two C 1s peaks of physically adsorbed carbon species (284.8 and 286.5 eV) (see Figure S4). The fine scan XPS spectra of CdS before and after NiCoP–NiCoPi loading are compared for S 2p, Cd 3d, and O 1s (Figure 3a–c). In the S 2p and Cd 3d spectra (Figure 3a,b), the binding energies of both S 2p and Cd 3d in NiCoP/Cds/NiCoPi are positively shifted, compared with those in CdS. The binding energies of S 2p shift from 161.33 and 162.52 to 161.53 and 162.75 eV, respectively; while the binding energies of Cd 3d shift from 404.98 and 411.74 to 405.07 and 411.87 eV, respectively. This result suggests that partial electrons were transferred from CdS, contributing to the formation of P=O=Si, which indicates the electronic interaction between CdS and cocatalysts. For the O 1s spectra, the bare CdS only shows a weak XPS peak at 532.2 eV, which is assigned to physically adsorbed oxygen species (Figure 3c). However, after the loading of the cocatalysts, a new intense peak at 531.1 eV is observed, which corresponds to the oxygen species in the phosphates. 50,51 Lattice oxygen from nickel and cobalt oxides with a binding energy of about 529.0 eV cannot be found, 52–54 indicating the absence of nickel and cobalt oxides in the sample.
For 5 mol % NiCoP/CdS/NiCoPi, the Ni 2p, Co 2p, and P 2p XPS spectra were also analyzed (Figure 3d–f). For the Ni 2p spectrum (Figure 3d), the intense peaks for Ni 2p3/2 are located at 853.4 and 856.5 eV, corresponding to Ni1+ and Ni2+ species, respectively. The Ni 2p1/2 region also shows two peaks at 869.6 and 874.8 eV because of the coexistence of Ni1+ and Ni2+, respectively. The XPS peaks at higher binding energies of 862.3 and 881.3 eV were assigned to the nickel satellite peaks. For the Co 2p spectrum (Figure 3e), a pair of XPS peaks with binding energies of 781.9 and 797.8 eV is attributed to Co2+; and the other pair at 777.9 and 793.0 eV is attributed to Co3+. The cobalt satellite peaks are found at 787.1 and 802.7 eV. In the P 2p XPS spectrum (Figure 3f), three peaks located at 129.1, 133.1, and 134.0 eV can be ascribed to P3−, PO43− (P5+), and PO3− (P5+), respectively, which confirms the simultaneous formation of phosphide and phosphate. Meanwhile, we also tested XPS for the used samples after three consecutive cycles (as shown in Figure S5). According to the atomic ratio from XPS before and after the reaction (Table S4), the relative content of P3− is basically unchanged after the reaction, while the contents of P5+, Ni, and Co become lower. This means that NiCoPi was partially photocorroded. The unchanged peak area for NiCoP indicates higher stability than that of NiCoPi. The distribution of the dual cocatalysts on CdS before and after the cycling test is schematically illustrated in Figure S6b. For dual-cocatalyst-loaded photocatalysts, photocatalytic activity was determined by the minority (i.e., NiCoP). Because NiCoPi was excessive, the partial loss of NiCoPi had little effect on hydrogen production. This probably explains that photocatalytic hydrogen evolution by NiCoP/CdS/NiCoPi did not decay after three consecutive cycles.

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The optical absorption of as-prepared bare CdS and 5 mol % NiCoP/CdS/NiCoPi, the Ni 2p, Co 2p, and P 2p XPS spectra were also analyzed (Figure 3d–f). For the Ni 2p spectrum (Figure 3d), the intense peaks for Ni 2p3/2 are located at 853.4 and 856.5 eV, corresponding to Ni1+ and Ni2+ species, respectively. The Ni 2p1/2 region also shows two peaks at 869.6 and 874.8 eV because of the coexistence of Ni1+ and Ni2+, respectively. The XPS peaks at higher binding energies of 862.3 and 881.3 eV were assigned to the nickel satellite peaks. For the Co 2p spectrum (Figure 3e), a pair of XPS peaks with binding energies of 781.9 and 797.8 eV is attributed to Co2+; and the other pair at 777.9 and 793.0 eV is attributed to Co3+. The cobalt satellite peaks are found at 787.1 and 802.7 eV. In the P 2p XPS spectrum (Figure 3f), three peaks located at 129.1, 133.1, and 134.0 eV can be ascribed to P3−, PO43− (P5+), and PO3− (P5+), respectively, which confirms the simultaneous formation of phosphide and phosphate. Meanwhile, we also tested XPS for the used samples after three consecutive cycles (as shown in Figure S5). According to the atomic ratio from XPS before and after the reaction (Table S4), the relative content of P3− is basically unchanged after the reaction, while the contents of P5+, Ni, and Co become lower. This means that NiCoPi was partially photocorroded. The unchanged peak area for NiCoP indicates higher stability than that of NiCoPi. The distribution of the dual cocatalysts on CdS before and after the cycling test is schematically illustrated in Figure S6b. For dual-cocatalyst-loaded photocatalysts, photocatalytic activity was determined by the minority (i.e., NiCoP). Because NiCoPi was excessive, the partial loss of NiCoPi had little effect on hydrogen production. This probably explains that photocatalytic hydrogen evolution by NiCoP/CdS/NiCoPi did not decay after three consecutive cycles.

PL ES was used to investigate photogenerated electron–hole recombination. Figure 4b shows the PL spectra of bare CdS and 5 mol % NiCoP/CdS/NiCoPi samples, measured at an excitation wavelength of 420 nm. Specifically, bare CdS nanorods show two strong emission peaks at 503 and 534 nm, assigned to the intrinsic and extrinsic emissions, respectively. After loading NiCoP–NiCoPi cocatalysts, there is no significant change in the positions of the emission peaks, while the intensity of these two peaks shows a dramatic decrease. The remarkable quenching of PL reveals that the cocatalysts had a striking effect on inhibiting the recombination of photogenerated electron–hole pairs. When photo-generated electron–hole pairs were generated in CdS, NiCoP and NiCoPi on the CdS surface acted as electron and hole capturers, respectively, alleviating the recombination of photogenerated charge carriers in CdS.

Electrochemical measurements were performed to further investigate the interface electron transfer and charge separation in bare CdS and 5 mol % NiCoP/CdS/NiCoPi (Figure 4c). EIS was carried out to test the surface resistance of two samples. In general, the smaller the radius of the arc in the EIS...
Nygquist plot, the lower the electron transfer resistance of the tested material, meaning that the interface charge transfer is faster. Obviously, 5 mol% NiCoP/CdS/NiCoPi shows a smaller surface resistance (i.e., a smaller EIS arc radius) than that of bare CdS, indicating that the loading of NiCoP–NiCoPi cocatalysts is beneficial for the separation and transfer of photogenerated electrons and holes. Meanwhile, a photocurrent test was performed in a three-electrode cell using bare CdS and 5 mol% NiCoP/CdS/NiCoPi as working electrodes under the irradiation of 420 nm light (Figure 4d). The photocurrent response of pristine CdS was very low, while that of NiCoP/CdS/NiCoPi was intensively enhanced, indicating that the modification of NiCoP and NiCoPi largely contributed to photogenerated carrier transportation and separation. What is more, EIS and photocurrent of NiCoPi were also tested for comparison, as shown in Figure S7 in Supporting Information. The result shows that NiCoP had a higher electron transfer resistance and lower photocurrent, compared with CdS and NiCoP/CdS/NiCoPi.

Photocatalytic hydrogen production by prepared samples was carried out under the irradiation of a 300 W xenon lamp equipped with a band cutoff filter (420 nm), using lactic acid as the sacrificial reagent. Lactic acid shows a higher hydrogen production efficiency than other sacrificial agents, such as TEOA and Na3S/Na2SO3 (see Figure S8). To confirm that the dual-cocatalysts, NiCoP and NiCoPi, synergistically contributed to photocatalytic activity, single-cocatalyst NiCoP or NiCoPi-modified CdS photocatalysts were prepared according to the method reported.25 Pure CdS and Pt loaded CdS samples were also used as reference for comparison. When a theoretical Pt loading content in Pt/CdS was 10 mol% (see Table S5 in Supporting Information), an actual loading content was measured to be 3.9 mol%. As shown in Figure 5a, the hydrogen evolution rate of NiCoP/CdS/NiCoPi (80.8 mmol·g⁻¹·h⁻¹) is about 202, 11, 4.7, and 7 times higher than that of CdS (0.4 mmol·g⁻¹·h⁻¹), Pt/CdS (7.6 mmol·g⁻¹·h⁻¹), 5 mol% NiCoP/CdS (17.1 mmol·g⁻¹·h⁻¹), and 5 mol% NiCoPi/CdS (11.9 mmol·g⁻¹·h⁻¹), respectively, indicating that the dual-cocatalysts played a more important role in photocatalytic hydrogen production than the single ones. Although various MP-decorated CdS photocatalysts have been investigated, to the best of our knowledge, the enhancement factor reported here (using pristine CdS as a reference) is extremely high (see Table S1 in Supporting Information).26 Interestingly, the HER rate of the NiCoPi/CdS/NiCoPi composite was much higher than the sum of those of NiCoP/CdS and NiCoPi/CdS. As we all know, only when photogenerated electrons and holes can be consumed equally and efficiently, considerable photocatalytic activity can be achieved. Therefore, a good photocatalytic system needs both oxidation and reduction cocatalysts. If there exists only a reduction cocatalyst that facilitates the consumption of photogenerated electrons, photogenerated holes are accumulated in CdS. These holes can easily combine with the electrons photogenerated later in CdS, or vice versa. Therefore, the coexistence of oxidation and reduction cocatalysts can have a synergetic effect in photocatalysis.

To explore the synergy between NiCoP and NiCoPi, the effect of NiCoP/NiCoPi ratio on photocatalytic activity was investigated for a fixed theoretical loading content of cocatalysts (i.e., 5 mol% NiCoP/NiCoPi). According to eq 2, more phosphine is generated from the phosphating reaction shown in Scheme 1, if more sodium hypophosphate is fed. By simply adjusting the [hypophosphate]/[metal precursor] ratio, the NiCoP/NiCoPi ratio was finely tuned. The ratio of NiCoP to NiCoPi (P⁵⁻/P³⁻) in the different samples measured by XPS increased gradually with the dose of sodium hypophosphate (see Figure S9a–d in Supporting Information). Photocatalytic hydrogen evolution was tested for NiCoP/CdS/NiCoPi prepared with varied [hypophosphate]/[metal precursor] molar ratios from 10 to 40. Photocatalytic activity increased first and then decreased with the increasing phosphide/phosphate ratio (P³⁻/P⁵⁻) (Figure S9e). The reason can be explained as follows. When a cocatalyst (NiCoP–NiCoPi) loading amount was too small, the hydrogen evolution activity increased with the cocatalysts loaded because of an increase of catalytic active spots, as illustrated in the first three panels of Figure S9f. However, photocatalytic activity decreased when the ratio of P³⁻/P⁵⁻ was increased to 30. This is because the excessive coverage of the cocatalysts could cause the direct contact between the reduction cocatalyst (NiCoP) and the oxidation cocatalyst (NiCoPi), forming recombination centers (as illustrated in the last panel of Figure S9f). In addition, the overloading of cocatalysts also blocked incident light, hindering the excitation and generation of photogenerated charge carriers.

Figure S5b shows the effect of the amount of dual-cocatalysts on photocatalytic activity. The optimal loading amount of the cocatalysts was 5 mol%, showing an average hydrogen evolution rate of 80.8 mmol·g⁻¹·h⁻¹. We also investigated the effect of the Ni/Co ratio on the hydrogen generation (Figure S10 in Supporting Information). When the Ni/Co ratio was changed from 1:2 to 2:1, the hydrogen production activity increased first and then dropped. The optimal Ni/Co ratio was around 1:1.

Photocatalytic hydrogen evolution by 5 mol% NiCoP/CdS/NiCoPi photocatalyst was tested under different wavelengths

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**Figure 5.** Photocatalytic performance: (a) hydrogen evolution rates of different samples (S1 = NiCoP, S2 = CdS, S3 = 3.9% Pt/CdS, S4 = 5% NiCoP/CdS, S5 = 5% NiCoP/CdS, and S6 = 5% NiCoPi/CdS/NiCoPi), (b) cocatalyst content (x mol%, x = 0, 1, 3, 5, 7, and 9)-dependent hydrogen evolution rates of the NiCoP/CdS/NiCoPi samples under visible light irradiation (λ > 420 nm). (c) AQE of 5 mol% NiCoP/CdS/NiCoPi under different wavelengths of monochromatic light irradiation, and (d) cyclic photocatalytic ability of the 5 mol% NiCoP/CdS/NiCoPi photocatalyst with prolonged visible light irradiation (λ > 420 nm) for 32 h.
of monochromatic light. The irradiation wavelength-dependent AQE was calculated according to eq 1. The AQE of Pt-loaded CdS was also tested for comparison, and the quantum efficiency of 3.95% (actual loading content) Pt/CdS was 1.93% at 420 nm. The AQE of NiCoP/CdS/NiCoPi at 420, 450, and 500 nm was 4S, 37, and 19%, respectively (Figure 5c). When the energy of incident light was smaller than the bandgap of CdS, the AQE became negligible, indicating that the absorption by the dual-cocatalysts in the range of 500–800 nm (Figure 4a) had little contribution to the hydrogen evolution.

It is well known that the durability of photocatalysts is essential for their practical application. Therefore, the cyclic stability of the photocatalyst was studied (Figure 5d). 5 mol % NiCoP/CdS/NiCoPi photocatalyst was subjected to three consecutive cycles of photocatalytic measurement, with each cycle lasting for 8 h. The experimental results showed that the catalyst still exhibited considerable hydrogen production activity during 24 h of testing. The decrease in activity during the second and third cycles is suspected to originate from the consumption of the sacrificial agent. A similar phenomenon was also observed for the bare CdS photocatalyst (Figure S11 in Supporting Information). To confirm this assumption, the photocatalyst was collected after the third cycle and a fresh sacrificial agent solution with the same concentration was used for a new cycle measurement. It was found that the hydrogen production recovered to the same level as the first cycle. However, for bare CdS, approximately 13% of photocatalytic hydrogen evolution activity could not be recovered because of the photocorrosion of CdS.58,59 All the above tests showed that NiCoP/CdS/NiCoPi exhibited both superior activity and stability to bare CdS.

To test the universality of the dual-cocatalyst system (NiCoP–NiCoPi), we performed the hydrogen production by the (NiCoP–NiCoPi) cocatalysts on another substrate, g-C₃N₄. As shown in Figure S12, by loading 5% cocatalysts (NiCoP–NiCoPi) on g-C₃N₄, the hydrogen production by NiCoP/g-C₃N₄/NiCoPi was also greatly improved (from 0 to 175 μmol·g⁻¹·h⁻¹).

It is generally accepted that freshly synthesized MPs experience a surface passivation after being stored in air, forming a thin layer of metal phosphates.33 Such a passivation layer can protect the MPs from further oxidation, and it can also be reversibly converted to their original state through reduction (so called surface activation) (Figure 6a). The hydrogen evolution mechanisms of the single- and dual-cocatalyst-modified CdS photocatalysts are proposed in Figure 6b,c, respectively. For the single-cocatalyst-modified CdS, the surface passivation layer is reduced by photogenerated electrons at the beginning of the photocatalytic process (step 1, Figure 6b). The activated NiCoP nanoparticles act as electron acceptors and hydrogen evolution sites. During the photocatalytic process, electrons that flow continuously from CdS to NiCoP nanoparticles will be eventually captured by protons adsorbed on the surfaces of the cocatalyst, generating hydrogen (Figure 6b), while the photogenerated holes left on the CdS surface will oxidize lactic acid (the sacrificial agent). This explains the performance enhancement of NiCoP/CdS, compared with bare CdS. Therefore, photocatalytic activity of the single-cocatalyst-modified CdS system is normally limited by sacrificial agent oxidation, which can be enhanced by the deposition of an oxidation cocatalyst (e.g., NiCoPi). The simultaneous loading of NiCoP and NiCoPi on the CdS forms a dual-cocatalyst-modified photocatalyst (Figure 6c), further promoting the photogenerated carrier separation. NiCoP nanoparticles act as the electron acceptor and hydrogen evolution cocatalyst, while NiCoPi electron donor and the cocatalyst for sacrificial agent oxidation. Only when the proton reduction rate matches the oxidation rate of the sacrificial agent, the hydrogen evolution will be maximized. This can be achieved by tuning the ratio between the reduction cocatalyst and the oxidation cocatalyst (see Figure S9).

In the field of electrolysis, MPs and metal phosphates are efficient hydrogen evolution electrocatalysts and oxygen evolution electrocatalysts, respectively.23–39 Using MPs for photocatalytic hydrogen evolution has been well established.23–33 Whether metal phosphates can act as oxygen evolution catalysts in photocatalytic systems is not clear. This is because the reduction half reaction would be restrained without the participation of the oxidation half reaction. However, for the dual-cocatalyst system, a hydrogen evolution rate of 233 μmol·g⁻¹·h⁻¹ was observed, indicating that NiCoPi as an oxidation cocatalyst was important in water splitting (see Figure S13 in Supporting Information).

To better explain the above experimental results and propose the photocatalytic mechanism of NiCoP/CdS/NiCoPi, the electronic band structure of NiCoP, NiCoPi, and CdS was studied. As shown in Figure S14 in Supporting Information, the bandgap energy (2.42 eV) of NiCoP/CdS/NiCoPi and CdS was obtained by UV–vis absorption spectroscopy. As shown in Figure S15 in Supporting Information, the conduction band (CB) of CdS, obtained from Mott–Schottky plots, was −0.72 V versus Ag/AgCl (−0.52 V vs NHE). According to Equation 4, the VB of CdS was −6.4 eV (vs vacuum level). Theoretical computation using density functional theory was conducted to derive the band structure and work function of NiCoP, from which NiCoP had metallic characteristic with nonzero density of states. 50

Figure 6. Diagram illustrating (a) surface passivation and activation of metal–phosphate, and photocatalytic hydrogen evolution by (b) single- and (c) dual-cocatalyst-modified CdS photocatalysts.
7b,c. stable hydrogen evolution is realized, as illustrated in Figure 7a-3. Thereafter, holes preferably migrate from CdS to NiCoPi because of the lower reduction potential of NiCoP, electrons are transferred from CdS to NiCoPi because of the lower oxidation potential of NiCoPi (Figure 7a-3). Thereafter, the reduction of protons and the oxidation of a sacrificial agent take place on the surface of the cocatalysts, and continuous and stable hydrogen evolution is realized, as illustrated in Figure 7b,c.

4. CONCLUSIONS

In summary, we developed a novel and efficient NiCoP/CdS/NiCoPi photocatalyst that incorporated both reduction and oxidation cocatalysts for photocatalytic hydrogen generation. The NiCoP–NiCoPi dual-cocatalysts were simultaneously deposited on CdS via a simple phosphating step using volatile decomposition products from sodium hypophosphate as the phosphorus source. The two distinct cocatalysts in contact with CdS facilitated electron and hole transfer to the corresponding acceptors. The photocurrent of NiCoP/CdS/NiCoPi enlarged significantly, compared with bare CdS, while its electrical impedance and PL emission decreased dramatically. The dual cocatalysts acted as reduction and oxidation sites for hydrogen evolution and sacrificial reagent oxidation, respectively. Upon the loading of dual cocatalysts, the visible-light-driven hydrogen evolution by CdS was greatly enhanced. The modified CdS with a cocatalyst loading content of 5 mol % showed a hydrogen evolution rate of 80.8 mmol·g⁻¹·h⁻¹, which was 202 times higher than that of bare CdS (0.4 mmol·g⁻¹·h⁻¹). It also exhibited remarkable durability for a continuous photocatalytic test with a total reaction time of 24 h. Finally, the work described here integrating a visible-light absorbing semiconductor with noble-metal-free reduction and oxidation cocatalysts opens up a viable strategy to the design of simple, robust, and cost-effective photocatalysts for solar fuel production.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c12790.

Comparison of some CdS-based photocatalytic systems using MPs as the cocatalysts for photocatalytic H₂ production in the literature; TG and DSC curves of sodium hypophosphate; thermal decomposition of sodium phosphate at different temperatures and flow rates of the carrier gas; ICP and DSC results of 5 mol % NiCoP/NiCoPi/CdS; theoretical and actual loading contents of NiCoP–NiCoPi, NiCoP, and NiCoPi in the 5% NiCoP/NiCoPi/CdS composite; XPS survey scan spectra of pure CdS and 5 mol % NiCoP/NiCoPi/CdS samples; XPS fine scan spectra of C 1s of pure CdS and 5 mol % NiCoP/NiCoPi/CdS samples; XPS fine scan spectra of S 2p, Cd 3d, O 1s, Ni 2p, Co 2p, and P 2p of 5 mol % NiCoP/NiCoPi/CdS after the photocatalytic reaction;
elemental ratios in 5 mol % NiCoP/NiCoPi/CdS before and after the reaction (from XPS); Nyquist plots from EIS and periodic on/off photocurrent response of NiCoP, CdS, and NiCoP/NiCoPi/CdS samples; XPS fine scan spectra of P 2p in 5 mol % NiCoP/CdS/NiCoPi prepared by different [hypophosphate]/[metal precursor] ratios; P3−/P5− XPS area ratio and hydrogen production activity of 5 mol % NiCoP/CdS/NiCoPi prepared by different [hypophosphate]/[metal precursor] ratios; hydrogen evolution by NiCoP/CdS/NiCoPi samples with different Ni−Co ratios under visible light irradiation (λ > 420 nm); cyclic photocellability of the CdS photocatalyst with prolonged visible light irradiation (λ > 420 nm) for 32 h; gas (H2, O2) evolution by NiCoP/CdS/NiCoPi for overall water splitting in the absence of a sacrifing agent; bandgap of pure CdS and 5 mol % NiCoP/NiCoPi/CdS samples; Mott–Schottky plots of CdS; and band structures and DOS of NiCoP (PDF).

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Notes
The authors declare no competing financial interest.

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