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Unique synergistic effects of ZIF-9(Co)-derived cobalt phosphide and CeVO₄ heterojunction for efficient hydrogen evolution

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ABSTRACT

The photocatalytic decomposition of water to produce hydrogen is an important process, through which solar energy can be converted to chemical energy. Non-precious metal phosphides have quietly attracted attention as an emerging inexpensive photocatalyst. In this study, we reported that a CoP/CeVO₄ hybrid photocatalyst exhibited high hydrogen evolution efficiency owing to EY (eosin Y) sensitization under visible light irradiation for the first time, and the amount of generated hydrogen reached 444.6 μmol in 5 h. The CoP/CeVO₄ nanohybrids were synthesized by a simple chemical precipitation method. The coupling of CoP and CeVO₄ with ZIF-9 as a precursor could be completed in one step. The CeVO₄ particles were firmly attached to the surface of the CoP particles to form a "small point" to "big point" heterojunction. The results of X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, EDX, and transmission electron microscopy showed the formation of CoP and CeVO₄ nanoparticles and the structure of the composite. Based on a detailed analysis of the Mott-Schottky plot, the UV-vis diffuse reflectance spectra, photocurrent-time (it) curve, Tafel curve, Nyquist curve (EIS), linear volt-ampere curve (LSV), and steady-state fluorescence spectra were studied. The time-resolved photoluminescence measurements indicated that the reason for the high-efficiency hydrogen evolution of CoP/CeVO₄ was that the bands of CoP and CeVO₄ were bent due to the existence of the Schottky barrier, and a heterojunction was formed between CoP and CeVO₄, which generated an internal electric field and accelerated the charge transfer. In addition, the synergistic effect between CoP and CeVO₄ provided a new hydrogen-evolution activity center for each of them. The improved carrier separation efficiency and the decrease in the photo-generated recombination rate led to the excellent photocatalytic hydrogen-evolution activity of the CoP/CeVO₄ composite catalyst. This work provides a new strategy for modulating the electronic structure and carrier behavior of transition metal phosphide photocatalysts.

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1. Introduction

As is well known, solar energy is clean and sustainable [1,2]. The efficient utilization of solar energy to solve the energy and

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environmental challenges experienced by human beings has become a very important research area in recent decades [3,4]. Semiconductor photocatalysis technology is considered a major discovery for artificial photosynthesis. Photocatalytic technology is an effective way to solve the growing problems of energy shortage and environmental pollution, which is attracting increasing attention [5–7]. As an ideal clean energy source, hydrogen has the advantages of a high combustion value and environmental friendliness [8–10]. Photocatalysis technology is one of the most developmental hydrogen production methods because it can be applied in the extraction of energy from sunlight, and it has simple operation requirements [11–14]. Therefore, the design and development of effective photocatalysts are crucial [15–17].

Since the photocatalytic hydrogen-evolution reaction (HER) is mostly a semi-reaction, it is necessary to introduce sacrificial reagents to compensate for this disadvantage [18–21]. Moreover, the presence of a photosensitizer accelerates the absorption of light by the photocatalyst [22–25]. Therefore, it is important to study the relationship between the structures and properties of photocatalyst materials. It is helpful to provide a guide for the development of low-cost, high-stability, and high-activity HER photocatalysts [26,27]. At present, eosin Y (EY) is used as a sensitizer for most catalysts, and it has proven to be a very good sensitizer [28,29]. Further, it has been found that EY-sensitized semiconductors have a high activity toward hydrogen evolution under visible light irradiation because the EY-sensitized photocatalyst can greatly promote the separation of electrons and holes. As effective promoters, transition metal phosphatides can improve the efficiency of the photocatalytic water splitting process for hydrogen production [30]. Transition metal phosphides include Ni_2P [31–33], CoP [34–36], FeP [37], MoP [38], WP [39], and Fe_2P [40]. Evidently, in the field of photocatalysis, few studies have been conducted on the hydrogen evolution performance of pure transition metal phosphides as the main catalyst.

In this study, we successfully synthesized pure CoP with ZIF-9 (Co-MOFs) as a precursor for the first time and prepared the CeVO_4 photocatalyst by simple chemical precipitation. The photocatalytic hydrogen production performances of CoP, CeVO_4 , and their composite catalysts were studied. The

CoP/ CeVO_4 composite catalyst was found to exhibit excellent photocatalytic activity under dye sensitization conditions. The results indicated that the composite photocatalytic activity of V1C1, with a mass ratio of 1:1, was optimal for hydrogen evolution when CoP and CeVO_4 were combined. The origin of the catalyst activity was further elucidated through a series of characterizations. It can be seen that after CoP and CeVO_4 were combined, due to the formation of a heterojunction, energy band bending occurred, which generated an internal electric field, which accelerated the rapid transfer of electrons and realized the synergy between CoP and CeVO_4 . The mutual provision of a new electronic active center between CoP and CeVO_4 greatly reduced the recombination of photogenerated charges. This work is expected to provide a strategy for modulating the photocatalytic electronic structure and carrier behavior of transition metal phosphides.

2. Experimental

2.1. Synthesis

2.1.1. Synthesis

The synthesis of Co-MOF (ZIF-9) was carried out according to the method described in the previous report [41]. In a typical synthesis, 0.23 g of benzimidazole and 0.28 g of $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 40 mL of ultra-pure water. After stirring for 15 min, 5 mL of ammonia water was added to the prepared solution. Subsequently, the solution was stirred continuously for 45 min and kept in the dark for 8 h. Finally, the product was centrifuged and washed with ethanol and ionized water more than three times.

2.1.2. The synthesis of CoP

In a typical preparation, 0.5 g of Co-MOF and 3 g of sodium hypo were uniformly mixed in a porcelain vessel. Thereafter, the mixture would be obtained at 300 °C in the N_2 atmosphere calcined 2 h with the heating rate of 3 °C/min. The black CoP samples obtained were washed with ethanol and ionized water several times and then dried at 80 °C overnight.

2.1.3. The synthesis of CeVO_4

Fig. 1. Schematic diagram of the catalyst synthesis.

Typically, 1 mmol of $\text{Ce}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ was dissolved in 20 mL of water, and a slightly transparent solution was obtained. Further, 1 mmol of NH_4VO_3 was dissolved in 40 mL of water, and a pale yellow solution was obtained at 60 °C. Afterward, NH_4VO_3 was added dropwise to the $\text{Ce}(\text{NO}_3)_2$ solution, and the solution was maintained at 90 °C in a constant-temperature water bath for 2 h. Finally, the solution was cooled naturally to room temperature, followed by centrifugation. The sediment was washed with ethanol and distilled water, and the products were dried in an oven at 80 °C.

2.1.4. Synthesis of CoP/CeVO₄ composite samples

The synthesis of the CoP/CeVO₄ composite sample was similar to that of the pure CeVO₄, except that in the synthesis of the pure CeVO₄ sample, CoP of a certain quality was added; afterward, the temperature was regulated using a water bath. According to the mass ratio of CeVO₄ and CoP, the compound catalysts were labeled as V1C3 ($m(\text{CeVO}_4):m(\text{CoP}) = 1:3$), V1C2 ($m(\text{CeVO}_4):m(\text{CoP}) = 1:2$), V1C1 ($m(\text{CeVO}_4):m(\text{CoP}) = 1:1$), V2C1 ($m(\text{CeVO}_4):m(\text{CoP}) = 2:1$), and C3V1 ($m(\text{CeVO}_4):m(\text{CoP}) = 3:1$). V represents the mass of CeVO₄, and C represents the mass of CoP. The specific steps, Step I and Step II, are indicated below.

2.2. Characterization

X-ray diffraction (XRD) measurement of the studied samples was carried out using an advance diffractometer operating (HORIBA Scientific, France) at 40 kV and 30 mA with a scan step width of 2θ from 10°–80° (10°/min). Energy-dispersive X-ray (EDX) analysis was performed using ESCALAB 250Xi. The morphology and microstructure of the photocatalyst samples were characterized by field emission scanning electron microscopy (FESEM, accelerated voltage: 5.0 kV) and transmission electron microscopy (TEM, accelerated voltage: 300 kV). (SEM: JSM-6701F. JEOL, TEM: FEI Tecnai TF20). The UV-vis diffuse reflectance spectroscopy (DRS) of the catalyst was performed using a UV-2550 (Shimadzu) spectrometer. BaSO₄ was used as the reference for the baseline correction. The Brunauer-Emmett-Teller (BET) surface areas were determined from the N₂ adsorption-desorption isotherms, which were recorded at 77 K on a Quantachrome Instrument (ASAP2020M). In a

standard three-electrode cell, the photoelectrochemical measurement was performed using an electrochemical analyzer (VersaStat4-400, Advanced measurement Technology, Inc). The supporting electrolyte was an aqueous solution of Na₂SO₄ (0.2 M). Photoluminescence (PL) spectroscopy was conducted using a FLUOROMAX-4 spectrophotometer at room temperature.

2.3. Photocatalytic hydrogen evolution experiments

A portion (10 mg) of the photocatalyst powder and 10 mg of EY were added into the sacrificial reagent (30 mL of TEOA aqueous solution (15 v/v%)). Prior to irradiation, the ultrasonic dispersion was performed for 5 min. Prior to the experiment, nitrogen was supplied to the system for 10 min until the air in the bottle was completely removed. The photocatalyst was maintained in the suspension constantly by magnetic stirring. A 5 W white light multichannel photocatalytic reaction system was used as the simulated solar light source. The amount of hydrogen produced was analyzed by gas chromatography (Tianmei GC7900, TCD, 13Xcolumn, N₂ as the carrier).

3. Results and discussion

3.1. XRD analysis

XRD analysis plays an important role in the study of the crystal structure of matter. Fig. 2(a) shows the XRD patterns of the pure CeVO₄ and pure CoP. The prepared diffraction peaks of CeVO₄ at $2\theta = 18.2^\circ, 24.0^\circ, 30.3^\circ, 32.4^\circ, 34.3^\circ, 39.1^\circ, 43.6^\circ, 47.9^\circ, 56.6^\circ, 60.2^\circ, 62.3^\circ, 67.9^\circ$, and 78.3° are attributed to the (101), (200), (211), (112), (220), (301), (103), (312), (004), (332), (204), (224), and (404) crystal faces in the standard card of CeVO₄ (JCPDS#12-757; space Group: I41/amd (no. 141); $a=b: 7.399$, $c: 6.496$), respectively. For the CoP prepared by completely phosphating ZIF-9, all the typical peaks located at $2\theta = 31.6^\circ, 35.3^\circ, 36.2^\circ, 46.2^\circ, 48.2^\circ, 52.3^\circ, 56.0^\circ, 56.8^\circ$, and 76.9° correspond to the (011), (200), (111), (112), (211), (103), (202), (301), and (222) crystal faces, and they can be indexed to CoP standard cards (JCPDS#65-1474; space group: Pnma (no. 62); $a: 5.077$, $b: 3.281$, $c: 5.587$). The reduction in the intensity of the CoP and CeVO₄ peaks indicates that the degree of

Fig. 2. XRD patterns of the CoP, CeVO₄, and V_nC_m samples ($n:m = 1:3, 1:2, 1:1, 2:1$, and $3:1$).

crystallization is relatively low, and the widening of the diffraction peak indicates that the size of the crystal is decreasing. Moreover, no other impurity peaks are observed in the XRD pattern, which means that the CeVO_4 and CoP products have high purities. This result is consistent with the results detected by subsequent EDX analysis. As shown in Fig. 2(b), in the $Vn\text{Cm}$ composite sample of CeVO_4 and CoP ($n:m = 1:3, 1:2, 1:1, 2:1$, and $3:1$), the diffraction peaks associated with CeVO_4 and CoP are observed. The diffraction peaks at $2\theta = 18.2^\circ, 24.0^\circ, 34.3^\circ$, and 47.9° in the $Vn\text{Cm}$ composite photocatalyst correspond to the crystal faces of (101), (200), (220), and (312) of CeVO_4 . The diffraction peaks at $2\theta = 31.6^\circ, 36.2^\circ, 46.2^\circ$, and 52.3° are the planes corresponding to (011), (111), (112), and (103) of CoP. Further, with the increase in the amount of CoP, the intensity of the crystal plane associated with CoP is enhanced; however, the crystallinity of the composite sample is reduced. We believe that the semi-crystalline state provides more electron transfer interfaces and active sites than highly crystalline states, which may be one of the reasons why the composite catalyst exhibits high catalytic activity in the sensitization system after the combination of CeVO_4 and CoP.

3.2. SEM and TEM

The surface characteristics and microstructure of the CoP, V1C1, and CeVO_4 photocatalysts were detected by SEM and TEM, as shown in Fig. 3(a–f). In addition, the elemental species contained in the V1C1 composite catalyst were also detected by EDX, as shown in Figs. 3(g) and 3(h). By testing the structure of the original CoP, it can be seen that CoP mainly exists as particles, which is well confirmed by SEM and TEM images, as shown in Figs. 3(a) and 3(b). As is clearly seen from Fig. 3(a), the pure CoP exhibits a particle stack structure, and it can be seen from Fig. 3(b) that it exhibits a distinct thin layer at the edge of the particle structure, which is similar to a small inter-sheet stack. The SEM and TEM images of the pure CeVO_4 are

shown in Figs. 3(c) and 3(d), and both of them indicate that CeVO_4 exists in the form of irregular nanoparticles. Combined with the XRD test, the poor crystallinity is the main reason for the non-uniform morphology of CeVO_4 . Compared with those of the original pure CoP and CeVO_4 , the morphology of the V1C1 composite sample is changed significantly, although the presence of CoP and CeVO_4 in the composite sample can still be clearly observed. Fig. 3(e) shows the SEM image of a composite sample of CoP and CeVO_4 . The analysis shows that the component with the relatively large particle size in the C1V1 composite photocatalyst is CoP, and the irregular particles on the surface of CoP are CeVO_4 . From Fig. 3(f), we can observe a similar phenomenon, which is the same as in Fig. 3(e), i.e., CeVO_4 and CoP are distributed uniformly and close to each other. As shown in Fig. 3(g), the lattice spacing ($d = 0.27 \text{ nm}$) in the C1V1 composite sample corresponds to the (112) crystal plane of CeVO_4 . Moreover, the presence of O, P, V, Co, and Ce in the V1C1 composite catalyst can be clearly observed from Fig. 3(h). Furthermore, the CoP and CeVO_4 content ratio is close to 1:1, as determined by semi-quantitative analysis of the surface atomic percentages. Fig. 3(i) shows the elemental species in V1C1. No other elements are found except for Co, P, Ce, V, and O, indicating that the synthesized composite catalyst has relatively high purity. The distribution of CoP and CeVO_4 can also be clearly observed from the distribution images of various elements in the element maps below, which is consistent with the results observed in the SEM and TEM images. Noticeably, CoP exhibits relatively large particles, while CeVO_4 exhibits relatively small particles that distribute uniformly on the surface of CoP, forming a firm attachment, such as that of "small point" to "big point." The original stacked structure of CoP becomes more dispersed in the V1C1 composite sample, which promotes the interaction of CeVO_4 and CoP so that more active sites can be exposed for more efficient hydrogen evolution. This means that the V1C1 sample is successfully synthesized.

Fig. 3. SEM and TEM images of CoP (a, b), CeVO_4 (c, d), and CoP/ CeVO_4 (V1C1) (e, f); HRTEM (g), element mapping (h), and EDX images (i) for V1C1.

Fig. 4. (a) XPS survey spectra of CoP, CeVO₄, and V1C1. High-resolution XPS spectra of Co 2p (b), P 2p (c), Ce 3d (d), V 2p (e), and O 1s (f).

3.3. XPS results

The composition and valence state of the surface chemical elements of the prepared CoP, CeVO₄, and V1C1 photocatalysts were studied by XPS. Fig. 4(a) reveals the full XPS spectra of the pure CoP, pure CeVO₄, and V1C1 composite, from which it can be seen that the composite contains certain elements, including Co, P, Ce, V, and O. Fig. 3(b) shows six different Co 2p peaks, and two of them, located at 793.7 and 802.9 eV, are assigned to Co 2p_{1/2}; the binding energy values of 778.7 and 785.7 eV correspond to Co 2p_{3/2}. In addition, the two diffraction peaks at 781.7 and 797.8 eV belong to the vibrational satellites of Co 2p_{3/2} and Co 2p_{1/2}, respectively [42–44]. In the V1C1 photocatalyst, the binding energies of P 2p at 130.1 and 133.4 eV belong to P 2p_{3/2} and phosphorus oxide species (P₂O₅ or PO₄³⁻), respectively. The binding energy at 129.2 eV is related to metal phosphide [45]. However, the binding energy of the P 2p_{3/2} orbital in pure CoP increases, indicating the change of the chemical bond or electron cloud density in CoP and CeVO₄ during the compounding process. Fig. 4(c) reveals the spectrum of Ce 3d, the shape of which is characteristic of Ce(III) valency. For Ce³⁺, the peaks at 881.9 and 885.8 eV correspond to the Ce 3d_{5/2} transition, and the peaks at 900.3 and 904.4 eV correspond to the Ce 3d_{3/2} binding energy. Furthermore, the binding energies at 885.8 and 904.4 eV represent the 3d₁₀4f₁ initial electronic state corresponding to Ce³⁺ [46]. No peak indicative of Ce⁴⁺ is found [47]. By comparing the binding energies of C1V1 and pure CeVO₄, it can be seen that the binding energy of the corresponding orbital in the composite C1V1 increases slightly. The XPS spectrum of the V 2p spectrum fitted curve (Fig. 4(e)) shows a result that can be ascribed to V⁵⁺ and

V³⁺. The binding energies of about 516.9 and 524.7 eV are attributed to V 2p_{3/2} and V 2p_{1/2} of V⁵⁺, respectively, and the binding energy of 523.3 eV is attributed to the V 2p_{1/2} track of V³⁺. The binding energy of V³⁺ does not change before and after the compound, while that of V⁵⁺ decreases slightly. In the O 1s spectrum in Fig. 4(f), there are two peaks at 529.8 and 531.7 eV. The former is attributed to the O²⁻ ion of the CeVO₄ lattice, and the latter is related to the O²⁻ ion of the V₂O₃ phase [48,49]. In the pure CeVO₄, the peak indicative of the O²⁻ ions dominates, and the V₂O₃ phase has relatively few O²⁻ ions, while the composite exhibits the opposite trend. By comparing the pure CoP, the XPS spectra of the pure CeVO₄ and CoP/CeVO₄ nanocomposites show that the binding energy of the metal cations (Co, Ce) increases, and the binding energies of the elements acting as anions decrease. These changes indicate a strong interaction between CeVO₄ and CoP, which can lead to the efficient migration of the photogenerated electrons between CeVO₄ and CoP.

3.4. BET characterization

To investigate the effect of the BET surface area on the photocatalytic activity, the nitrogen adsorption-desorption isotherm was tested at 77 K. The pore volume, pore size, porosity, and nitrogen adsorption-desorption isotherms were determined, and they are shown in Table 1, and Fig. 5 are photo-

Table 1

Parameters of CeVO₄, V1C1, and CoP obtained from the analysis of N₂.

Sample	S_{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average pore size (nm)
CeVO ₄	124	0.28	8
V1C1	51	0.18	17
CoP	11	0.06	20

Fig. 5. (a) N₂ isothermal adsorption curves of CeVO₄, V1C1, and CoP. (b) BJH adsorption mean pore-size distributions of the samples.

catalytic activity. The shapes of the isotherms of the pure CeVO₄, pure CoP, and V1C1 nanocomposites shown in Fig. 5(a) are almost identical to the shape of the type IV isotherm. An H3 hysteresis loop can be observed at a relatively high pressure (0.6–1.0), which means that there is a multilayer adsorption process for the mesoporous material due to capillary condensation, which is consistent with the pore-size distribution curve in Fig. 4(b). The specific surface area of the V1C1 composite nanostructure is between that of the pure CeVO₄ and that of the pure CoP. The specific surface areas of the CeVO₄, V1C1, and CoP nanomaterials are 124, 51, and 11 m²g⁻¹, respectively. The difference in density between CeVO₄ and CoP and their respective specific surface areas per unit mass are the main reasons for the change in the specific surface area of the final compo-

site. The average pore sizes of CeVO₄, V1C1, and CoP are 8, 17, and 20 nm, respectively. The average pore size increased after the loading of CoP on CeVO₄. The pore volume measured by BJH shows that the pore volumes of the CeVO₄, V1C1, and CoP nanomaterials are 0.28, 0.18, and 0.06 cm³g⁻¹, respectively.

3.5. Photocatalytic hydrogen evolution activity of the catalyst

Fig. 6 shows the photocatalytic hydrogen evolution performance of all the prepared samples using a 15 v/v% triethanolamine as the sacrificial reagent. As is clearly observed in Fig. 6(a), the pure CeVO₄ exhibits very weak photocatalytic hydrogen-evolution activity. The pure CoP initially exhibited a certain photocatalytic hydrogen evolution activity. However, the pho-

Fig. 6. (a) Hydrogen evolution amount over different catalyst samples. (b) Hydrogen evolution amount over binary photocatalyst samples with different quality ratios of CeVO₄/CoP. (c) Hydrogen production rate of V1C1 (10 mg, 5 h) in different pH TEOA solutions. (d) Comparison of the hydrogen production of the V1C1 samples in different EY mass changes (in TEOA with pH = 9, 5 h).

togenerated electron-hole recombination rate of the pure CoP at a later stage was relatively high, which inhibited the hydrogen evolution and generalization of its photocatalytic hydrogen considerably. The hydrogen generation activities of CeVO₄ and CoP are significantly improved. Fig. 6(b) shows the total hydrogen production of the composite catalyst with different ratios of CeVO₄ and CoP in 5 h. It can be seen from the figure that the V1C1 composite catalyst with a CeVO₄ and CoP ratio of 1:1 has the highest hydrogen production, reaching 444.6 μmol in 5 h. Fig. 6(c) shows the effect of pH value on the hydrogen release activity of the V1C1 composite catalyst. V1C1 exhibits different selectivities based on the reaction environment. V1C1 has the best catalytic activity (pH = 11) in a weak alkaline environment. A mild alkaline environment is the most favorable factor for hydrogen evolution systems. However, peracid or over-base is not conducive for the progress of HER, mainly due to the protonation of triethanolamine with the increase in acidity, which leads to the weakening of the electron donation ability of triethanolamine. When the alkalinity is at a relatively high value, the H⁺ content in the system is remarkably lowered, which is thermodynamically unfavorable for the photocatalyst precipitation of hydrogen in the reaction system [50]. Fig. 6(d) shows a photocatalytic hydrogen production performance of 10 mg of the V1C1 composite catalyst, and different amounts of EY were investigated at pH = 9. As can be seen from the figure, EY has a significant influence on the catalytic activity of the hydrogen evolution. As the amount of EY added to the reaction system increases, the amount of hydrogen produced increases significantly, which demonstrates that the addition of 10 mg EY does not satisfy all the active sites that are exposed to the catalyst and promotes sensitization. When the dye molecules are added in excess, the amount of hydrogen reduces gradually, which means that some active sites are overly covered. Due to the shielding effect of EY, the generation of hydrogen is suppressed. In addition, excess dye molecules can be used to filter input light, which can cause the self-quenching of the excited dye molecules and even lead to the loss of light and dye decomposition [51]. This indicates that an appropriate amount of dye is very important for enhancing the catalytic activity of the catalyst in the dye sensitization system.

The cyclic stability of the photocatalyst is very important for

Fig. 7. Hydrogen production cycle over the C1V1 photocatalyst.

its application. As shown in Fig. 7, the stability of the V1C1 composite photocatalyst is tested under the same conditions. The sacrificial reagent is not changed throughout the experiment. It can be seen from the stability test that the V1C1 sample has a highly efficient photocatalytic activity during the first cycle. However, the hydrogen production amount begins to decline during the second cycle. When 10 mg of EY is resupplied to the reaction bottle, the hydrogen production activity is immediately recovered, and the amount of produced hydrogen becomes higher than the total amount of hydrogen generated at the end of the first cycle. Combined with the hydrogen production activity of the catalyst in Fig. 6(c), it is evident that the decrease in the hydrogen production in the second cycle is caused by the decomposition of the EY molecule under long-term illumination. Therefore, EY is supplied in the third cycle. The post-hydrogen production is immediately restored, and the subsequent decrease in the hydrogen production activity in the fourth cycle is retarded.

3.6. UV-vis DRS and photoluminescence analysis

The optical properties of the CeVO₄, CoP, and V1C1 composite photocatalysts were tested by UV-vis DRS. When the optical properties of the pure CeVO₄, pure CoP, and V1C1 photocatalysts were investigated, the collected spectra were converted into the Kubelka-Munk function of $\varphi(r)$ versus wavelength. The observed results are shown in Fig. 8. The Kubelka-Munk transformation is used to convert the reflection measurements to the absorption spectra:

$$\varphi(r) = \frac{(1-r)^2}{2r} = \frac{A(\lambda)}{S(\lambda)} \propto \alpha = \frac{(h\nu - E_g)^n}{h\nu}$$

$\varphi(r)$ = Kubelka-Munk/re-emission function;

r = diffuse reflectance of the sample;

$A(\lambda)$ = absorption coefficient;

$S(\lambda)$ = scattering coefficient;

h is Planck's constant, 4.136×10^{-15} eV;

c is the velocity of light velocity, 2.997×10^{17} nm/s;

n is the value of the integer; λ is the wavelength, nm; E_g is the bandgap energy.

According to the Kubelka-Munk method, the accurate optical band gap, E_g , can be estimated [46]. Namely, the value of E_g can be obtained by plotting $(ah\nu)^{1/2}$ as a function of the photon energy ($h\nu$). From the pure CeVO₄ to V1C1, it is observed that the absorption edge of the catalyst exhibited a redshift. According to the calculation, the bandgap of CeVO₄ is 2.34 eV. Furthermore, the light absorption capacity of the V1C1 binary composite catalyst is significantly improved. In fact, in the photocatalytic reactions based on visible light excitation, only photogenic electrons from the conduction band can participate in the hydrogen generation reaction. In this case, with the decrease in the bandgap and the increase in the light absorption capacity, the photocatalytic utilization capacity of the photocatalyst and hydrogen production activity can be improved.

The fluorescence performance of the photocatalyst in the EY solution was tested by steady-state fluorescence spectroscopy to further study the photoelectron transfer performance. The

Fig. 8. (a) UV-vis DRS spectra of CeVO_4 , V1C1, and CoP; (b) illustrations for the Kubelka-Munk transform spectra for CeVO_4 , V1C1, and CoP.

catalysts in the EY solution were denoted as EY- CeVO_4 , EY-CoP, and EY-V1C1, respectively. The catalyst in the EY aqueous solution was excited by light with a wavelength of 480 nm. Once the catalyst electrons reach the excited state, they jump back to the ground state, and the energy is released as fluorescence. The steady-state fluorescence spectra of EY, CeVO_4 , CoP, and V1C1 samples are shown in Fig. 9(a), and the peak wavelength is 536 nm. After the sample is irradiated with light of a certain energy, the nano-compound is triggered, and the electrons in the ground state absorb energy and jump from the low energy level to the higher energy level so that an exciton separation occurs and photogenerated electron-hole pairs are generated [52]. Since the electrons in the excited state were unstable, they returned to the ground state by a radiative transition, and the decay of the radiative transformation process was accompanied by the emission of fluorescent photons. In this process, a large number of EY molecules in the excited state transition returned to the ground state, resulting in fluorescence emission peaks. As shown in Fig. 9(a), the pure EY solution generated the strongest fluorescence. When CeVO_4 , CoP, and V1C1 were sensitized by EY, the fluorescence intensity decreased sharply, particularly the V1C1 composite photocatalyst, reaching the minimum value. This phenomenon can be explained as follows:

different fluorescence intensities indicate different electron-hole recombination degrees. When the fluorescence intensity is high, the peak value is high, indicating that the number of excited electrons returning to the ground state through the transformation of radioactive decay is high. This leads to a high electron-recombination rate. On the contrary, for different composites, the fluorescence intensities of different materials gradually decrease, indicating that the number of electrons converted by radiation decreases. The weakening of the fluorescence emission peak indicates that the photoelectron and hole recombination is inhibited considerably in the composite catalyst.

To further understand the interaction between the excited dye EY and the catalyst, the lifetimes of EY, EY- CeVO_4 , EY-CoP, and EY-V1C1 were determined by transient fluorescence spectroscopy. The attenuation curve obtained is fitted with the following formula:

$$I(t) = B + Ae^{-\frac{t}{\tau_1}}$$

It can be clearly observed from Fig. 9(b), that the fitting attenuation curves of EY, EY- CeVO_4 , EY-CoP, and EY-V1C1 with a single exponential function have lifetime values of 0.4140, 0.4061, 0.3911, and 0.3862 ns, respectively. Therefore, it

Fig. 9. Steady-state (a) and transient fluorescence spectra (b) of CeVO_4 , CoP, and C1V1.

Fig. 10. i-t curves (a) and LSV curves (b) of CeVO₄, V1C1, and CoP.

means that the V1C1 catalyst has the highest transfer rate of photogenerated charge, and the highest photocatalytic activity of hydrogen evolution, which is consistent with the results of hydrogen evolution kinetics and photoelectrochemical measurements.

3.7. Photoelectric performance test

To explore the charge state of the semiconductor catalyst before and after the illumination, the transient photocurrent responses of the pure CeVO₄, pure CoP, and the C1V1 composite catalyst were tested. As shown in Fig. 10(a), all the catalysts exhibited different photocurrent responses under intermittent illumination. The photocurrent intensity of all the photocatalysts increased significantly under irradiation. The V1C1 sample showed the best photocurrent response. In other words, due to the loading of CeVO₄, the constructed CoP/CeVO₄ heterojunction could improve the efficiency of the electron separation, transfer, and photocatalytic decomposition of hydrogen production.

In addition, to further compare the photocatalytic hydrogen evolution activity, the sample polarization curve was tested by linear sweep voltammetry to evaluate the hydrogen production activity of the catalyst. Fig. 10(b) shows the polarization curves of the catalysts, CeVO₄, V1C1, and CoP. Noticeably, V1C1 exhibits a higher current density and lower hydrogen evolution overpotential than pure CoP and pure CeVO₄. This indicates that V1C1 is a promising hydrogen evolution catalyst. The LSV measurement results and transient photocurrent response

indicate that the V1C1 composite catalyst exhibits an excellent photoelectrochemical activity.

EIS can be measured to assess the difficulty of the charge-transfer process. The Nyquist curve of the original measurement is shown in Fig. 11(a). The radius of the Nyquist curve reflects the mass transfer rate of the charge in the interfacial reaction. A semicircular curve with a small radius indicates that the charge can be transferred rapidly [12]. As can be seen from Fig. 11(a), CoP shows the smallest Nyquist curve, indicating the rapid transfer of electrons. It is also shown, from the side, that CoP is an excellent cocatalyst, which can greatly improve the catalytic performance of the composite catalyst. Compared to the case with the pure CeVO₄, the curve radius of the composite catalyst (V1C1) reduced after loading with CoP on the surface of pure CeVO₄, and the electron transfer ability was enhanced.

The corresponding Tafel plot was recorded in the low current density region to understand the interaction between CeVO₄ and CoP. The Tafel slope was used to study the kinetics of the HER process. Fig. 11(b) shows the Tafel plot of the CeVO₄, C1V1, and CoP electrodes. The Tafel slope (b) is determined by fitting the linear portion of the HER polarization curve to the Tafel equation [49,53].

$$\eta = a + b \log |i|,$$

where η is the overpotential; a is the intercept; b is the Tafel slope; and i is the current density.

As shown in Fig. 11(b), the corresponding Tafel slopes of CeVO₄, C1V1, and CoP are ~128, ~73, and ~115 mV dec⁻¹, re-

Fig. 11. (a) Nyquist curves, (b) Tafel curves of CeVO₄, V1C1, and CoP; (c) the adsorption and desorption process model of water dissociation reaction on CoP.

spectively. The Tafel slope of C1V1 was observed to be ~ 73 mV dec $^{-1}$, which is much lower than CeVO $_4$ (~ 128 mV dec $^{-1}$) and CoP (~ 115 mV dec $^{-1}$). Conventionally, the HER occurs in two steps on the surface of the catalyst, which include the adsorption and desorption processes of water molecules on the catalyst surface, with considering the CoP structure as an example, the reaction steps of the hydrogen separation are shown in Fig. 11(c). The reaction steps can be categorized based on control steps into the Volmer step, Heyrovsky step, and Tafel step. The Volmer reaction is a proton adsorption step, also called an electrochemical step; the Heyrovsky reaction is an electrochemical desorption step; the Tafel reaction is a complex desorption step [26]. The general reaction follows the Volmer–Heyrovsky mechanism or the Volmer–Tafel mechanism, which is controlled by the relative rate of the reaction of each step [27]. The relevant reactions are as follows:

The Tafel slope falls within the range of 40–120 mV dec $^{-1}$, indicating that HER on C1V1 and CoP occurs via the Volmer–Heyrovsky mechanism, and the Heyrovsky step is the rate-controlled step [28]. When the Tafel slope is greater than 120 mV dec $^{-1}$, the Volmer step is the main step controlling the reaction speed [29]. Notably, the introduction of CoP causes a significant slope decrease in the Tafel slope of the C1V1 composite catalyst. This low overpotential and small Tafel slope indicate that C1V1 results in an excellent HER efficiency and its kinetic conditions are superior to those of the other catalysts.

The Mott–Schottky equation is used to evaluate the flat band potential (E_{fb}) of the pure CeVO $_4$, pure CoP, and V1C1 [26,54].

$$\frac{1}{C^2} = \frac{2}{\epsilon e \epsilon_0 N_a} \left[(E - E_{fb}) - \frac{KT}{e} \right],$$

where e is the electron charge;

K is Boltzmann constant;

ϵ_0 is the vacuum permittivity;

T is the absolute temperature;

N_a is the acceptor concentration;

E is the electrode applied potential;

ϵ is the dielectric constant of CoP, V1C1, and CeVO $_4$;

and C is the capacitance of the space charge region.

As shown in Figs. 12(a) and 12(b), the negative slope of the C^{-2}/E diagram represents a p-type semiconductor, and the positive slope represents an n-type semiconductor. Relative to SCE, the E_{fb} of the pure CeVO $_4$ and pure CoP are -0.73 and -0.06 V, respectively. Therefore, according to the meaning of the flat band potential, the Fermi level (E_F) positions of the pure CeVO $_4$ and CoP samples can be estimated approximately, and the Fermi level of the n-type semiconductor is closer to the conduction band. For the composite catalyst, V1C1, of CeVO $_4$ and CoP, there are two linear regions in the Mott–Schottky figure, which could be attributed to the flat band potential of the composite of CeVO $_4$ and CoP, whose values are -0.65 V and -0.22 V, respectively. This is due to the heterostructure formed by the n-type semiconductor (CeVO $_4$) and the n-type semiconductor (CoP). The Fermi energy levels of different semiconductor catalysts move to the same level, which results in a shift of the flat band potential [13]. Generally, the conduction band potential (E_{CB}) of an n-type semiconductor is more negative than its flat band potential of about -0.1 or -0.2 V [52], i.e.,

$$E_{CB} = E_{fb} - 0.1 / E_{CB} = E_{fb} - 0.2$$

Therefore, the E_{CB} estimates for CeVO $_4$ and CoP are -0.93 and -0.26 V with respect to SCE, relative to the common hy-

Fig. 12. Mott–Schottky plots of CeVO $_4$ (a), CoP (b), and V1C1 (c); (d) energy band structure of the catalysts.

Fig. 13. Mechanism diagram of the hydrogen production process by water decomposition of EY-sensitized C1V1.

drogen electrode (E_{NHE}) of -0.69 and -0.02 V, respectively.

$$E_{\text{NHE}} = E_{\text{SCE}} + 0.241 \text{ V}$$

The valence band (E_{VB}) potentials of the pure CeVO_4 and pure CoP are 1.65 and 1.3 V, respectively, calculated by the following equation relative to NHE [16]:

$$E_{\text{VB}} = E_{\text{CB}} + E_{\text{g}}$$

According to the above formula, it is also possible to calculate the position relation of the valence band of the V1C1 compound agent, as shown in Figs. 12(c) and 12(d).

3.8. Possible photocatalytic mechanism

Based on the above results, the reaction process of the photocatalytic decomposition of water, which produces hydrogen gas, can be inferred in the EY-sensitized CoP/ CeVO_4 heterojunction system. Dye molecules are adsorbed on the surface of the CoP/ CeVO_4 structure to form a single excited state EY^{1*} under the condition of visible light irradiation; thereafter, the system is converted to form a more stable three-excited state, EY^{3*} . As the donors accept electrons, TEOA is restored, and the formation of quenching EY^- induces a relatively strong reducing ability [13,14]. The EY^- electron is transferred to the active surface of the C1V1 composite catalyst, thereby generating hydrogen through the reduction reaction; meanwhile, the dye molecules return to the ground state. For the CoP and CeVO_4 semiconductors, there are piles of reducing electrons on the conduction band, which create oxidized holes on the valence band after being excited by light. When CoP and CeVO_4 interact closely, the electrons on the conduction band of CoP at a low level undergo reduction to generate hydrogen gas. However, after CoP and CeVO_4 are recombined, CoP loses electrons and thus gains positive charges, while the edge of the conduction band bends upward due to the loss of electrons. The edge of the conduction band of CeVO_4 bends downward due to the accumulation of electrons; consequently, the electrons in the conduction band of CeVO_4 are transferred to the conduction band of CoP, thereby enhancing the photocatalytic hydrogen-production activity of the composite catalyst [48]. Different from the traditional type I heterojunction, the valence band edge of CeVO_4 bends downward, and the valence band edge of CoP bends upward. Therefore, the photogenerated holes can-

not be transferred from the valence band of CeVO_4 to the valence band of CoP; only oxidation occurs in their valence bands. This ensures the reduction and oxidizing ability of the photo-generated electrons and holes, thereby improving the photocatalytic activity of the composite photocatalyst. The C1V1 composite catalyst exhibits excellent dye adsorption and electron acceptability; consequently, the recombination of the photogenic charge can be greatly reduced. Therefore, the photocatalytic hydrogen-production efficiency of the composite catalyst can be improved. The chemical reaction process corresponding to the whole process of hydrogen production can be expressed as follows:

4. Conclusions

In summary, we proposed a novel CeVO_4 -modified CoP photocatalyst. The obtained CoP/ CeVO_4 hybrid photocatalyst exhibited excellent photocatalytic activity under visible light irradiation ($444.6 \mu\text{mol H}_2$ in 5 h). The composite material (CoP/ CeVO_4) showed a good photocatalytic hydrogen evolution rate, which was up to 98.8 more than that of pure CeVO_4 and 2.3 times that of pure CoP. In addition, the composite displayed a high photocurrent, small charge transfer resistance, and low overpotential. The excellent photocatalytic performance of CoP/ CeVO_4 depended on the formation of a heterojunction between CeVO_4 and CoP, which promoted the efficient charge carrier separation and led to a high separation efficiency, in addition to a low recombination rate of the photogenerated electron-hole pairs. Our work provides an effective method for the development of metal phosphides for dye-sensitized hydrogen photocatalysts.

Conflicts of interest

The authors declare no competing interests.

Author contributions

Lijun Zhang conceived and designed the experiments; Zhi-liang Jin and Xuqiang Hao contributed reagents/materials and analysis tools; and Lijun Zhang wrote the paper; Junke Li and

Graphical Abstract

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Unique synergistic effects of ZIF-9(Co)-derived cobalt phosphide and CeVO₄ heterojunction for efficient hydrogen evolution

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The excellent photocatalytic performance of CoP/CeVO₄ depends on the formation of a heterojunction between CoVO₄ and CoP, which promotes efficient charge carrier separation and leads to a high separation efficiency and low recombination rate of the photogenerated electron-hole pairs.

Yuanpeng Wang assisted in the testing of the experiment.

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ZIF-9(Co)衍生物磷化钴复合CeVO₄协同高效产氢性能

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摘要: 众所周知, 太阳能是一种清洁、可持续的能源。如何更有效地利用太阳能来解决人类面临的能源和环境问题已成为近几十年来科研工作者的研究热点。半导体光催化技术被认为是人工光合作用的主要发现。光催化技术是解决日益严重的能源短缺和环境污染问题的有效途径, 越来越受到人们的关注。氢作为理想的清洁能源, 具有燃烧价值高, 无污染的优点。光催化制氢技术的应用是最具发展性的制氢方法之一。因此, 有效光催化剂的设计和开发显得十分重要。

由于光催化析氢反应(HER)主要是半反应, 因此必须引入牺牲试剂。同时, 光敏剂的存在加速了光催化剂对光的吸收。在这种情况下研究光催化材料的结构和性质之间的关系至关重要, 它能指导人们开发低成本、高稳定性、高活性的析氢光催化剂。本文首次成功地合成了以ZIF-9(Co-MOFs)作为前驱体的CoP纳米粒子, 并通过简单的化学沉淀法制备了CeVO₄光催化剂。深入研究了CoP, CeVO₄及其复合催化剂的光催化制氢性能。发现CoP/CeVO₄复合催化剂在染料敏化条件下表现出优异的光催化活性。当CoP和CeVO₄结合质量比为1:1时, 所得样品V1C1的复合光催化活性对于析氢最佳, 在5 h内氢产生量达到444.6 μmol。由于CeVO₄和CoP偶联是一步完成。CeVO₄牢固地粘附在CoP颗粒的表面上, 形成“小点”到“大点”异质结。XRD, XPS, SEM, EDX和TEM的结果显示, CoP和CeVO₄纳米颗粒的形成和复合物的结构。基于对Mott-Schottky曲线, UV-vis漫射光谱, 光电流-时间曲线, Tafel曲线, 奈奎斯特曲线, 线性伏安曲线和稳态/瞬态荧光测量结果表明, CoP/CeVO₄高效析氢的原因是CoP和CeVO₄复合后存在肖特基势垒, 导致能带发生弯曲, 并且CoP与CeVO₄之间异质结所形成的内建电场能加速电荷转移。此外, CoP和CeVO₄之间独特的协同效应为彼此提供了新的析氢活性中心。提高了载流子分离效率, 降低了光生载流子复合率。因此, CoP/CeVO₄复合催化剂具有优异的光催化析氢活性。本文为过渡金属磷化物光催化剂的电子结构和载流子行为的调控提供了新的策略。

关键词: 光催化; CoP; CeVO₄; 染料敏化; 产氢

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