One-step preparation of cobalt phosphate at room temperature for effective photocatalytic H₂ evolution

Xing Liu^{1,2} · Hua Lai^{1,2} · Junhua Li^{1,2} · Gang Peng^{1,2} · Rongying Zeng¹

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Abstract

Cobalt phosphate materials were prepared in the present work in one step at room temperature using different raw materials and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and N₂ gas adsorption. Cobalt phosphates exhibit 3D flower-like structures, and the assembly of nanosheets (petals of the “flowers”) of cobalt phosphate prepared with sodium phosphate and cobalt acetate as raw materials (denoted as Co-P(A)) is more incompact than that of cobalt phosphate prepared with diammonium hydrogen phosphate and cobalt nitrate as raw materials (denoted as Co-P(B)) due to the former’s mildly basic environment. The cobalt phosphates show relatively high photocatalytic activity for H₂ evolution reaction (HER) in the presence of Eosin Y as a sensitizer in an aqueous triethanolamine solution. The activity of Co-P(A) (0.40 mmol h⁻¹ g⁻¹) exceeds that of Co-P(B) (0.19 mmol h⁻¹ g⁻¹), which can be attributed to a more dispersive nanosheet and larger BET-specific surface area of Co-P(A). The mechanisms of photocatalytic HER and the formation of flower-like Co₃(PO₄)₂ were discussed. The present system comprising of only abundant elements contributes toward the development of cost-efficient solar HER to achieve sustainable development.

Graphical abstract

Keywords Cobalt phosphate · Photocatalysis · Hydrogen

1 Introduction

H₂ fuel is one of the ideal green energy carriers. Photocatalytic splitting of water into H₂ is a promising approach to obtain H₂ [1–4]. A photo-hydrogen conversion system generally includes a sensitizer, a H₂ evolution reaction (HER) catalyst, and an electron donor (sacrificial agent). Transition metal (e.g., Ru and Rh) complexes are classical and frequently used sensitizers due to their high efficiency [5–7]. In recent years, xanthenes (e.g., eosin Y, erythrosine) are

✉ Xing Liu
liuxing1127@sina.com

¹ College of Chemistry and Materials Science, Hengyang Normal University, Hengyang 421008, China

² Key Laboratory of Functional Metal-Organic Compounds of Hunan Province and Key Laboratory of Functional Organometallic Materials of College of Hunan Province, Hengyang Normal University, Hengyang 421008, China

promising organic photosensitizers for H_2 evolution from water splitting because of their low cost and ready availability [8–10].

Pt is considered to be the best choice for HER catalysts because of its low overpotential and exceptional activity [11–13]. However, as a noble metal, Pt is substantially limited in applications due to its scarceness and expensiveness. Thus, the development of highly active, stable catalysts containing only earth-abundant elements is an essential objective.

Phosphorus-based transition metal compounds have been applied in the field of photocatalytic HER. For example, nickel, cobalt, and iron phosphides can catalyze HER in the photocatalysis processes [14–17]. However, exploring low cost and relative highly efficient HER photocatalysts remains challenging.

Transition metal phosphates show highly structural stabilities and good electron-mediating capabilities [18]. These phosphates had been widely used as catalysts for environmental or energy conversions, especially in oxygen evolution reaction (OER) [18–20]. For example, in 2008, Nocera found that cobalt phosphate film prepared by electrodeposition is an excellent electrocatalyst for H_2O oxidation [21]. Zhang et al. investigated the influence of coordination environment on OER activity and found that tetrahedral Co sites in the anhydrous $Co_3(PO_4)_2$ has high activity because the high oxidation state cobalt (hydr)oxide, as an active intermediate, is readily generated in the OER process [22]. The flexible coordination nature of the phosphate group can stabilize the intermediate states of central transition metals, ensuring it an efficient redox change [23, 24]. Theoretical chemistry also reveals that the phosphate group is important in proton transportation, which is a key step in transition metal phosphates catalyzed OER. This group also possesses durability and high catalytic activity and can act as strong electron mediators. Thus, transition metal phosphates are potential photocatalysts for HER. To date, a few works focus on the photocatalytic HER of transition metal phosphates. Prof. Das reported that reduced graphene oxide (RGO) sheets modified flower-like $Co_3(PO_4)_2$ composites system with enhanced photocatalytic efficiency for water splitting; the photo-induced electron from $Co_3(PO_4)_2$ transfers to the RGO, thus reducing the hole–electron recombination [25].

In the present work, cobalt phosphates were prepared in one step under room temperature using different raw materials. The cobalt phosphates show relatively high photocatalytic activity for HER using Eosin Y as a sensitizer and triethanolamine (TEOA) as a sacrificial electron donor. The present work is a meaningful attempt on cobalt phosphate as photocatalysts for HER from the viewpoint of dye sensitization.

2 Experimental

2.1 Chemicals

Cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$), sodium phosphate ($Na(PO_4)_3 \cdot 12H_2O$), diammonium hydrogen phosphate ($(NH_4)_2HPO_4$), cobalt acetate ($Co(CH_3COO)_2 \cdot 4H_2O$), 2, 4, 5, 7-tetrabromofluorescein disodium salt (Eosin Y), NaOH, HCl, and TEOA were purchased from Sinopharm Group Chemical Reagent Co. Ltd. (Shanghai, China). The chemicals were of analytical grade and were used without further purification.

2.2 Preparation of cobalt phosphate

Cobalt phosphate was synthesized by simple precipitation methods using different raw materials. Sodium phosphate (2.0 mmol) and cobalt acetate (3.0 mmol) were dissolved in 40.0 mL H_2O to obtain solutions A and B, respectively. A was drop-wisely added into B under stirring at room temperature. Afterward, the reaction system continued stirring for 2 h to realize complete precipitation. The solid was separated by suction filtration, washed with water and ethanol, and dried at 80 °C for 5 h. The produced cobalt phosphate was labeled as Co-P(A).

Diammonium hydrogen phosphate and cobalt nitrate were used as raw materials. The same above procedures were conducted to obtain cobalt phosphate, which was labeled as Co-P(B).

2.3 Photocatalytic H_2 evolution

Photocatalytic reaction was carried out in a Pyrex cell at room temperature. 100.0 mg cobalt phosphate. A total of 80.0 mL aqueous TEOA (2.0×10^{-3} mol L^{-1}) solution (its pH was adjusted as 7.0 with HCl), and a certain Eosin Y(EY) were added in the cell. The above mixture formed a suspension system by ultrasonic dispersion. N_2 was bubbled through the cell before irradiation to replace the air. A 250 W Hg lamp with a 420 nm cut-off-filter was used as the light source. The produced H_2 was measured on a GC equipped with a TCD and molecular sieve column.

2.4 Characterization

XRD was measured using the D8 ADVANCE polycrystalline X-ray diffractometer (Bruker, Germany) with Cu $K\alpha$ radiation as the X-ray source. SEM images were obtained from an SU8020 (HITACHI, Japan) with a working voltage of 30 kV. X-ray photoelectron spectroscopy (XPS) was obtained on the ESCALAB250xi photoelectron spectrometer (Thermo Scientific) using monochromatized Mg $K\alpha$

X-Ray resource (150 W) with $C 1 s = 284.8$ eV as an internal reference. N_2 gas adsorption/desorption isotherms were measured on the ASAP 2460 nitrogen adsorption apparatus (Micromeritics Instruments, USA).

3 Results and discussion

3.1 Characterization of cobalt phosphates

The XRD patterns of as-prepared cobalt phosphates were shown in Fig. 1. The two samples are well crystallized and exhibit almost the same diffraction peaks during from 10° to 58° (2-theta), and all the diffraction peaks reveal that a pure monoclinic phase of $Co_3(PO_4)_2 \cdot 8H_2O$ (PDF #041-0375) was obtained [25, 26]. The FWHMs of (020) plane for Co-P(A) and Co-P(B) are 0.248° and 0.182° , respectively, and their mean crystallite sizes are 31.9 and 43.5 nm, respectively, which were calculated by the Scherrer equation based on the (020) plane. The crystallite size of Co-P(A) is smaller than that of Co-P(B), implying that the former could offer an additional surface to generate HER active sites.

The morphologies of Co-P(A) and Co-P(B) were investigated by SEM (Fig. 2). The images revealed the 3D flower-like structures of Co-P(A) and Co-P(B) with cobalt phosphate petals (nanosheets) with thicknesses of 40–150 nm. The nanosheets of Co-P(A) resembles are more incompact than that of Co-P(B), possibly implying that Co-P(A) is more dispersive and possesses a higher specific surface area than Co-P(B). The EDS displayed the elemental composition of the of Co-P(A) and Co-P(B) (Table 1), and the relative contents of Co, P, and O are remarkably similar for the two samples.

Fig. 1 XRD patterns of cobalt phosphates

Figure 3 shows the XPS spectra of Co-P(A) and Co-P(B). As shown in Fig. 3a, Co-P(A) and Co-P(B) contain O, P, and Co, and almost identical XPS spectra for all the elements. The characteristic peaks of Co 2p are revealed in Fig. 3b, the deconvoluted XPS spectra of Co 2p_{3/2} show that the cobalt is in the +2 state, with representative peaks located at 782.2 and 786.0 eV. The small peak with a binding energy at 781.0 eV corresponds to Co(III) and its satellite peak is absent. Again, the peaks of Co 2p_{1/2} appears at 797.9 eV and 803.1 eV, which is consistent with the results of Co(II)-containing phosphates [18, 25]. As shown in Fig. 3c, the peaks of P 2p_{1/2} and P 2p_{3/2} appear at 133.9 eV and 133.1 eV, respectively, which corresponds to PO_4^{3-} . The O 1s XPS spectrum shown a strong peak with the center at 531.3 eV, which is attributed to oxygen ion from PO_4^{3-} . Besides, a shoulder peak at higher binding energy (532.7 eV) can be observed, implying the adsorption of oxygen species (H_2O) [27]. The above results confirmed that the Co-P(A) and Co-P(B) are $Co_3(PO_4)_2 \cdot 8H_2O$ and they have the same compositions and chemical states of the elements. Moreover, the elements analysis based on the XPS was presented in Table 2, the Co and P become more than that from the EDS, may implying more Co and P atoms locates on the surfaces in the $Co_3(PO_4)_2 \cdot 8H_2O$ materials, and which is beneficial for the HER since Co and P play key role in the HER process [27].

Figure 4 shows the N_2 adsorption–desorption isotherms of Co-P(A) and Co-P(B). The N_2 adsorption on Co-P(A) and Co-P(B) is slight at low pressure ($p/p_0 < 0.3$). A remarkable adsorption occurs at a relative pressure region ($p/p_0 > 0.7$) on the Co-P(A), while a certain adsorption appears only at a high relative pressure region ($p/p_0 > 0.9$) on the Co-P(B). An obvious hysteresis loop can be observed for the isotherm of Co-P(A) but that of Co-P(B) is not obvious, and the hysteresis loop may be attributed to the capillary condensation of macro-porous structures causing by the stacking of the nanosheets and flower-like structures of Co-P(A) [28]. This result is in agreement with the SEM results in which Co-P(A) is more dispersive. The BET-specific surface areas of Co-P(A) and Co-P(B) are $15.78 \text{ m}^2/\text{g}$ and $6.80 \text{ m}^2/\text{g}$, respectively, which is also in accordance with XRD and SEM analyses. Compared with Co-P(B), Co-P(A) with a larger specific surface area should provide more active sites for HER.

3.2 HER properties

The photocatalytic HER properties of Co-P(A) and Co-P(B) were tested with EY as a sensitizer upon visible light illumination. As shown in Fig. 5, EY-sensitized Co-P(A) and Co-P(B) exhibit remarkable HER activities, while no H_2 is found without EY. This phenomenon suggests that cobalt phosphate itself cannot produce hydrogen under visible

Fig. 2 SEM images of (a, b) Co-P(A) and c, d Co-P(B)

Table 1 Elemental concentration of Co-P(A) and Co-P(B) from EDS

Sample	Element (at%)		
	O K	P K	Co K
Co-P(A)	75.18	11.51	13.31
Co-P(B)	73.97	11.58	14.55

light, and the HER is driven by dye sensitization. The activity of Co-P(A) ($0.40 \text{ mmol h}^{-1} \text{ g}^{-1}$) is higher than that of Co-P(B) ($0.19 \text{ mmol h}^{-1} \text{ g}^{-1}$). This result can be attributed to a more dispersive nanosheets and larger BET-specific surface area of Co-P(A).

EY was repeatedly used as an efficient photo-sensitizer for photocatalytic HER in our previous works [8, 12, 16]. EY can effectively yield triplet excited $^3\text{EY}^*$ through intersystem crossing (ISC) after absorption of visible light, because of its electronic donor–acceptor (D–A) structure

and the heavy atom effect of bromines. $^3\text{EY}^*$ is prevalently quenched by TEOA to become radical $\text{EY}\cdot^-$. The produced $\text{EY}\cdot^-$ is a highly active species, and its reductive potential is -0.8 V (vs. NHE) [16]. Meanwhile, the conduction band (CB) potential of $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ is -0.73 V [25]. Thus, the electron transfer from the $\text{EY}\cdot^-$ to $\text{Co}_3(\text{PO}_4)_2$ is thermodynamically feasible. $\text{EY}\cdot^-$ can readily obtain regeneration after providing the surplus electron to the cobalt phosphate catalyst. The cobalt phosphate with accepted electron immediately reduces H^+ (from H_2O) into hydrogen. Co-P(A) is more dispersive than Co-P(B), thus providing more reaction active sites for HER and displaying a higher activity. A possible HER mechanism was shown in Fig. 6.

The influences of EY concentration, pH, dosage of $\text{Co}_3(\text{PO}_4)_2$, and electron donors on HER were investigated. Figure 7 (A) shows the influence of EY concentration on photocatalytic HER. The HER activity increases with the EY

Fig. 3 XPS spectra (a) total survey, b Co2p, c P2p, d O1s of Co-P(A) and Co-P(B)

Table 2 Elemental concentration of Co-P(A) and Co-P(B) from XPS

Sample	Element (at%)		
	O1s	P2p	Co2p
Co-P(A)	65.56	14.55	19.89
Co-P(B)	65.10	14.98	19.90

concentration firstly and then reduces with the highest activity of $0.40 \text{ mmol} \cdot \text{h}^{-1} \text{ g}^{-1}$ at $2.0 \times 10^{-4} \text{ mol L}^{-1}$ EY. When EY increases from 0 to $2.0 \times 10^{-4} \text{ mol L}^{-1}$, the energy antenna effect (light-absorb ability) is increasing boosted, ultimately resulting in an enhanced HER. However, a concentration quenching occurs due to the collisional deactivation of the $^3\text{EY}^*$ when the EY concentration is excessively high, thus leading to a lowered HER activity. As shown in Fig. 7B, the pH of photocatalytic HER system strongly influences on the activity. No hydrogen was produced at pH 5, and the activity is maximum at pH 8. TEOA must undergo protonation of N atoms at acidic conditions, and the protonated TEOA does not give its electrons on N atoms, [8, 29] that is, it no longer functions as an electron donor. The weakened HER activity may be caused by low-level H^+ in the aqueous

Fig. 4 Nitrogen adsorption–desorption isotherms of Co-P(A) and Co-P(B)

solution at strong basic conditions ($\text{pH} > 8$). Therefore, the highest activity appears at pH 8. Figure 7C shows the H_2 evolution rate with different $\text{Co}_3(\text{PO}_4)_2$ dosages. No H_2 was observed when the system only includes EY and TEOA,

Fig. 5 Photocatalytic H₂ production using Eosin Y sensitized cobalt phosphate. Conditions: 0.10 g cobalt phosphate, 2×10^{-4} mol L⁻¹ Eosin Y, 2×10^{-3} mol L⁻¹ TEOA, light source: 250 W high pressure Hg lamp, $\lambda > 420$ nm

Fig. 6 Schematic representation of possible mechanism of photocatalytic HER

suggesting that $\text{Co}_3(\text{PO}_4)_2$ as catalysts is indispensable for photocatalytic HER. The HER activity is enhanced with the increase in $\text{Co}_3(\text{PO}_4)_2$ dosage, reaching a maximum with 100 mg catalysts. Further increase in $\text{Co}_3(\text{PO}_4)_2$ dosage leads to a decreased HER activity, probably because additional $\text{Co}_3(\text{PO}_4)_2$ particles can bring about incident light shielding. As shown in Fig. 7D, some different sacrificial electron donors, including TEOA, trimethylamine, methanol, EDTA, were investigated. As widely used electron donor, methanol displays no evolved hydrogen in this system. The activities of H₂ generation decrease in order of TEOA > trimethylamine > EDTA. Thus, TEOA is selected as a sacrificial electron donor in this work.

The stability of photocatalytic HER over EY-sensitized Co-P(A) was shown in Fig. 8. The activity of EY-sensitized Co-P(A) displays some declining trend in the second and third runs. The decreased activity might be as a result of the degradation of EY; for example, the loss of -Br from EY typically results in a lower HER activity with irradiation time. This phenomenon was observed and demonstrated by previous studies [13, 16, 30]. The SEM and XRD of the Co-P(A) after the three runs of HER experiment were measured to prove its stability during photocatalytic HER. As shown in Fig. 9, the morphology and crystallinity of the Co-P(A) catalysts are maintained, suggesting its sustainability under in the long-run.

3.3 Discussion on generation of $\text{Co}_3(\text{PO}_4)_2$

As depicted in Fig. 10, the generation of flower-like $\text{Co}_3(\text{PO}_4)_2$ structures involves the following four stages: [26, 31, 32] the nucleation process, the growth of nanoparticles, the formation of nanosheets by oriented attachment, and the generation of flower-like structures via self-assembly of the nanosheets. $\text{Co}_3(\text{PO}_4)_2$ precipitation is generated when PO_4^{3-} was added into the Co^{2+} aqueous solution. The basicity of sodium phosphate is stronger than that of diammonium hydrogen phosphate, and cobalt acetate is stronger than cobalt nitrate, which leads to a slower precipitation between PO_4^{3-} and Co^{2+} in the case of Co-P(A). [25] The morphology of characteristic nanosheets, including Ostwald ripening, the dissolution of fine crystals, and the growth of larger ones, is expressed as a nonhomogeneous growth. Then, these nanosheets gradually turn more substantial and abundant and form flower-like structures of $\text{Co}_3(\text{PO}_4)_2$ by self-assembly. The nanosheets of Co-P(A) resembles are more incompact than that of Co-P(B) due to mildly basic environments resulting from acetate ion, generating more dispersive Co-P(A) nanosheets and higher photocatalytic HER activity.

4 Conclusions

Cobalt phosphates with 3D flower-like structures were prepared in one step at room temperature using different raw materials. The nanosheets (petals of flower-like structures) of Co-P(A) resembles are more incompact than that of Co-P(B) due to mildly basic environments. The cobalt phosphates show relatively high photocatalytic activity for HER using Eosin Y as a sensitizer. The activity of Co-P(A) ($0.40 \text{ mmol h}^{-1} \text{ g}^{-1}$) is higher than that of Co-P(B)

Fig. 7 Impact of (A) concentration of EY, B pH of photocatalytic system, C dose of Co-P(A), and D electron donor on HER activity

Fig. 8 Time course of photocatalytic hydrogen evolution over Eosin Y sensitized Co-P(A)

($0.19\ mmol\ h^{-1}\ g^{-1}$), which can be attributed to a more dispersive nanosheets and larger BET-specific surface area of Co-P(A).

Fig. 9 A XRD and B SEM of Co-P(A) after the three runs HER experiment

Fig. 10 Mechanism of the formation of flower-like $\text{Co}_3(\text{PO}_4)_2$

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Author contributions XL: Methodology, writing—original draft preparation; HL: Writing—reviewing and editing; GP: Formal analysis; JL: Funding acquisition; RZ: Software.

Date availability The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Conflict of interest The authors have no conflicts to disclose.

Consent to participate All authors gave their consent to participate.

Consent for publication All authors gave their consent to publish.

Ethics approval Not applicable.

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