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Article

Functional principle of the synergistic effect of co-loaded Co-Pi and FeOOH on Fe₂O₃ photoanodes for photoelectrochemical water oxidation

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ABSTRACT

The establishment of multi-component catalytic systems on Fe₂O₃ photoanodes presents considerable potential for significantly enhancing the performance of photoelectrochemical water splitting systems. In this study, we hydrothermally synthesized a Fe₂O₃ photoanode. In addition, d-FeOOH synthesized via dip-coating and hydrothermally prepared h-FeOOH were used as cocatalysts and their synergistic combinations with cobalt phosphate (Co-Pi) were investigated. The synergy between h-FeOOH and Co-Pi was remarkable, whereas that between d-FeOOH and Co-Pi was negligible. For example, the onset potentials of the Co-Pi/h-FeOOH and Co-Pi/d-FeOOH dual catalysts, were cathodically shifted by 270 and 170 mV, respectively. Moreover, the photocurrent density of the Co-Pi/h-FeOOH/Fe₂O₃ anode was significantly higher than that of the Co-Pi/d-FeOOH/Fe₂O₃ one. The synergistic effect of Co-Pi and h-FeOOH could be attributed to the significantly inhibited recombination of surface charges owing to the formation of a p-n junction between β-FeOOH and Fe₂O₃ and the large contact area between the granular h-FeOOH and Co-Pi. However, the thin amorphous FeOOH layer of the Co-Pi/d-FeOOH/Fe₂O₃ anode acted as a hole-transfer medium, and weakly promoted the kinetics of the charge transfer process.

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1. Introduction

The conversion of solar energy to hydrogen fuel *via* photoelectrochemical (PEC) water splitting is considered to be a potential solution for the current global energy crisis and environmental problems [1]. The overall efficiency of the water splitting process is limited by the water oxidation process, which involves four electrons [2]. Owing to its favorable bandgap of 2.0–2.2 eV, high durability in aqueous and oxidative environments, and high natural abundance, α-Fe₂O₃ (hematite) stands out as one of the most promising water splitting pho-

toanodes [3,4]. Theoretically, the photocurrent density of Fe₂O₃ photoanodes could exceed 12 mA cm⁻², when assisted by an applied bias of 0.3–0.4 V [5,6]. However, in practice, the photocurrent density of as-prepared Fe₂O₃ photoanodes is lower than 3 mA cm⁻². This is mostly attributed to the low mobility of carriers (<0.1 cm² V⁻¹ s⁻¹) [7] and the sluggish oxygen evolution reaction (OER) kinetics, which are affected by the surface states [8,9]. The PEC performance of Fe₂O₃ could be improved by using nanostructured Fe₂O₃ [10,11] and foreign element doping [12]. However, the onset potential of doped nanostructured Fe₂O₃ photoanodes could still be as high as ~0.9 V

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[13,14], which is much higher than that of other photoanode materials, such as BiVO₄ [15] and TiO₂ [16], and represents a major drawback.

The use of OER catalysts for PEC water splitting has been demonstrated to ameliorate this problem by passivating the photoanode surface and/or accelerate the OER kinetics [17–19]. Most Earth-abundant OER catalyst materials comprise transition metal compounds, such as cobalt phosphate (Co-Pi) [20,21], nickel borate, Ni or Co oxides [22,23], Ni or Fe oxyhydroxides [24–26], and their complex oxides/oxyhydroxides [27,28]. Currently, research efforts are focused on achieving synergistic effects using dual catalysts. For example, Co-Pi/Co₃O₄ [29] and F:FeOOH/FeNiOOH [28] were determined to show a synergistic effect on the lowering of the onset potential of Fe₂O₃ photoanodes. In addition Ni(OH)₂/IrO₂ [17] and C dots/Co₃O₄ dual catalysts [30] were reported to present synergistic effects mostly on the photocurrent rather than the onset potential. Hence, the functional selection and assembly methods of the cocatalysts could be very important to simultaneously achieve the decrease in onset potential and increase in photocurrent.

In this study, Co-Pi and FeOOH were successively deposited on nanostructured Fe₂O₃ photoanodes in an attempt to decrease their onset potential and increase their photocurrent. Furthermore, the effects of Co-Pi combined with layered amorphous (d-FeOOH) and granular (β-FeOOH; h-FeOOH) FeOOH on the performance of the photoanodes were different. A strong synergistic effect was observed when the Co-Pi/h-FeOOH dual catalyst was used, whereas the synergistic effect of Co-Pi/d-FeOOH was negligible. The difference in the functional effects of the combinations of Co-Pi with the two types of FeOOH was explained from a kinetic perspective. This study aimed to analyze the effects of the prospective assembly of dual catalysts on lowering the onset potential of Fe₂O₃ photoanodes.

2. Experimental

2.1. Materials

Sodium hydroxide (NaOH, 98%), hydrochloric acid (37%), cobalt nitrate (98%), ferric chloride (97%), ammonium fluoride (98.0%), monopotassium phosphate (98%), and ferrous sulfate heptahydrate (FeSO₄·7H₂O, 98%), were purchased from Sinopharm Chemical Reagent Co., Ltd., and were used as received without further purification. Fluorine-doped tin oxide (FTO)-coated glass (surface resistivity of ~7 Ω sq⁻¹) was purchased from Huanan Xiangcheng Tech. Co.

2.2. Material synthesis

Fe₂O₃ and Co-Pi were synthesized using the procedure outlined in one of our previous reports [21]. A Fe₂O₃ sample was used for the hydrothermal synthesis of h-FeOOH/Fe₂O₃, and the reaction time was optimized to 1 h. Conversely, d-FeOOH was coated on Fe₂O₃ via dip-coating, as described in the literature [31]. In brief, a Fe₂O₃ anode was immersed in a 5 mM

FeSO₄·7H₂O aqueous solution, it was maintained at 40 °C for 10–30 min, and then it was washed and dried. The dip-coating time was optimized to 10 min.

2.3. Photoelectrochemical measurements

Photoelectrochemical testing was performed using a CHI 660D (CH Instruments) electrochemical workstation with three-electrode configuration which consisted of Hg/HgO (1 M KOH) and a 1 × 3 cm² Pt sheet as the reference and counter electrodes, respectively; 1.0 M NaOH aqueous solution (pH 13.6) was used as the electrolyte [32,33]. The polarization curves were obtained at 20 mV s⁻¹ under simulated sunlight illumination obtained using a Xe lamp (PLS-SXE300D, Perfect-Light) equipped with an AM 1.5G filter. The light intensity was measured to be 100 mW cm⁻².

The incident photon-to-current conversion efficiencies (IPCEs) at the bias of 1.23 V vs. the reversible hydrogen electrode (RHE) were calculated by changing the bandpass filters of the Xe lamp in the range of 350–700 nm and using the following equation:

$$\text{IPCE} = (1240J)/(\lambda \cdot J_{\text{light}}) \quad (1)$$

where J is the photocurrent density, λ is the incident light wavelength, and J_{light} is the measured power density of the incident light (100 mW cm⁻²) [34].

The produced H₂ and O₂ were collected and detected using a 6890D (Agilent) gas chromatograph equipped with a thermal conductivity detector and molecular sieve 5A column. N₂ was used as the carrier gas (flow rate of 36 mL min⁻¹), and the oven and detector temperatures were 50 and 120 °C, respectively.

All potentials were referenced to the RHE using the Nernst equation [35]:

$$V_{\text{RHE}} (\text{V}) = V_{\text{Hg/HgO}} (\text{V}) + 0.113 + 0.059 \text{ pH} \quad (2)$$

The applied bias photo-to-current conversion efficiency (ABPE) was estimated using the following formula [30]:

$$\text{ABPE} = J \times (1.23 - |V_{\text{RHE}}|)/J_{\text{light}} \times 100\% \quad (3)$$

Mott-Schottky (MS) experiments were carried out at the interval of 50 mV under 10 kHz in the dark, and the carrier density (N_d) was calculated as follows:

$$N_d = 2/[q\epsilon\epsilon_0 d(1/C_s^2)/dV] \quad (4)$$

where C_s is the capacitance, V is the applied bias, q is the unit electron charge, ϵ_0 is the vacuum permittivity, and ϵ is the relative permittivity of Fe₂O₃.

The open circuit potential (OCP) decay curves were obtained under light irradiation before the light was turned off. The OCP values under light irradiation and in the dark were recorded when equilibrium was reached after the light was turned on/off.

Potential electrochemical impedance spectroscopy (PEIS) was performed in the range of 100 kHz to 0.1 Hz under AM 1.5G illumination at the amplitude of 20 mV by varying the applied bias.

2.4. Characterization

X-ray diffraction (XRD) patterns were obtained using a D8 Advance, (Bruker) diffractometer equipped with a Cu Kα radi-

tion source. Raman spectra were acquired using a FV-CFR-A (Zolix) laser Raman microscope spectrometer with the excitation wavelength of 532 nm. The morphology of the materials was analyzed using a FEI Nova 200 (NanoLab) field emission scanning electron microscopy (FESEM) instrument and a JEM-2100F (JEOL) transmission electron microscopy (TEM) apparatus. An L750 (PerkinElmer) ultraviolet-visible (UV-Vis) spectrometer in diffuse reflection mode was used to acquire the absorption spectra of the samples. Furthermore, the X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) profiles of the samples were obtained using an ESCA PHI 1600 (Physical Electronics) system with Al K_{α} X-ray excitation source and an ESCALAB 250 Xi (Thermo Scientific) device, respectively.

3. Results and discussion

3.1. Material characterization

The crystal phase structure of the electrodes is investigated using XRD and the patterns are compared, as shown in Fig. 1a. The strong peaks of SnO_2 originated from the FTO substrate, and the peaks of the synthesized FeOOH were indexed to the tetragonal β - FeOOH phase (akaganeite-Q, JCPDS No. 34-1266). The peaks of calcined β - FeOOH were indexed to the hexagonal α - Fe_2O_3 (hematite, JCPDS No. 33-0664) phase with (110) preferred orientation. The peaks of α - Fe_2O_3 dominated the XRD patterns of the samples that contained FeOOH and/or Co-Pi.

The formation of β - FeOOH was confirmed by the presence of the enlarged peak in the XRD profile of h- $\text{FeOOH}/\text{Fe}_2\text{O}_3$, which was ascribed to the (301) plane of β - FeOOH (Fig. 1b). However, the characteristic peaks of FeOOH were absent from the XRD profile of the d- FeOOH sample, which indicated that only an insignificantly small amount of FeOOH was present in this sample or that FeOOH formed an amorphous layer. Raman spectroscopy was used to analyze the surface composition of the electrodes more in depth. The typical Raman peaks of FeOOH were present in the spectra of both $\text{FeOOH}/\text{Fe}_2\text{O}_3$ samples, which confirmed the successful deposition of FeOOH on Fe_2O_3 (Fig. 1c). [36]. The optical properties of the samples were analyzed using their UV-Vis diffuse reflection spectra (Fig. 1d). The absorption edges of β - FeOOH (550 nm) and Fe_2O_3 (600 nm) indicated that their bandgaps were 2.35 and 2.15 eV respectively, as illustrated in the Tauc plots (Fig. S1). The absorption of d- FeOOH was negligible, whereas the light absorption of the h- $\text{FeOOH}/\text{Fe}_2\text{O}_3$ composite sample slightly increased at 550 nm.

As observed from the SEM images (Fig. S2), the as-prepared Fe_2O_3 shows the same coralline-like nanostructure we have previously reported [14,19]. No apparent changes in surface morphology were identified after d- FeOOH or h- FeOOH were loaded on the surface of Fe_2O_3 , and this was likely attributed to the small loading amounts. Co-Pi appeared to fill the interspaces of the nanostructures, which resulted in the rough surfaces of the samples. The high-resolution TEM images of the bulk d- $\text{FeOOH}/\text{Fe}_2\text{O}_3$, h- $\text{FeOOH}/\text{Fe}_2\text{O}_3$, Co-Pi/d- $\text{FeOOH}/\text{Fe}_2\text{O}_3$, and

Fig. 1. (a) X-ray diffraction (XRD) patterns of β - FeOOH , bare Fe_2O_3 , d- $\text{FeOOH}/\text{Fe}_2\text{O}_3$, h- $\text{FeOOH}/\text{Fe}_2\text{O}_3$, Co-Pi/ Fe_2O_3 , Co-Pi/d- $\text{FeOOH}/\text{Fe}_2\text{O}_3$, and Co-Pi/h- $\text{FeOOH}/\text{Fe}_2\text{O}_3$; (b) Expanded XRD patterns of β - FeOOH , bare Fe_2O_3 , d- $\text{FeOOH}/\text{Fe}_2\text{O}_3$, and h- $\text{FeOOH}/\text{Fe}_2\text{O}_3$; (c) Raman spectra and (d) ultraviolet-visible diffuse reflection spectra of bare Fe_2O_3 , β - FeOOH , d- $\text{FeOOH}/\text{Fe}_2\text{O}_3$, and h- $\text{FeOOH}/\text{Fe}_2\text{O}_3$. Here Co-Pi denotes cobalt phosphate.

Co-Pi/h-FeOOH/Fe₂O₃ (Fig. 2) revealed that the interplanar fringe distances were 0.368 and 0.270 nm, which corresponded to the (012) and (104) planes of Fe₂O₃, respectively. The surface of bare Fe₂O₃ is also presented in Fig. 2c. The surface of Fe₂O₃ was covered with FeOOH for both FeOOH/Fe₂O₃ samples; however, the surface morphologies of the FeOOH/Fe₂O₃ samples were different: d-FeOOH formed a 3–4 nm thick uniform amorphous layer on the surface of Fe₂O₃ (Fig. 2a), and the appearance of the h-FeOOH deposited on the surface of Fe₂O₃ was granular (Fig. 2b). The lattice fringe spacing of h-FeOOH was 0.333 nm, which coincided with that of the (310) plane of β -FeOOH. In addition, both the Co-Pi/d-FeOOH/Fe₂O₃ and Co-Pi/h-FeOOH/Fe₂O₃ samples presented $\sim$ 5 nm thick Co-Pi amorphous layers (Figs. 2d and e). The energy-dispersive X-ray spectroscopy maps and Co and P XPS profiles of the Co-Pi/d-FeOOH/Fe₂O₃ sample confirmed the presence of Co-Pi (Fig. S3). In addition, it was revealed that Co²⁺ and Co³⁺ ions coexisted in Co-Pi. The electrochemically active surface areas (ECSAs) of Fe₂O₃, d-FeOOH/Fe₂O₃ and h-FeOOH/Fe₂O₃ were estimated according to their electrochemical double-layer capacitances (*C_{dl}*) (Fig. S4). The ECSA of the d-FeOOH layer coating on the surface of Fe₂O₃ was thinner than that of the bare Fe₂O₃ sample, but no differences existed between the ECSAs of the bare and h-FeOOH-coated Fe₂O₃ samples, which indicated that the ECSA of the h-FeOOH nanoparticles was larger than that of the layered d-FeOOH.

3.2. Photoelectrochemical performance

The polarization (*J*-*V*) curves of the bare and modified Fe₂O₃ photoanodes are compared (Fig. 3a), and the turn-on voltage (*V_{on}*) is estimated using the traditional linear extrapolation method [37]. The *V_{on}* of the bare Fe₂O₃ anode was as high as

0.92 V vs. RHE and its photocurrent density was 0.85 mA cm⁻² at 1.23 V vs. RHE. After optimization, d- and h-FeOOH loadings contribute to shifting *V_{on}* by 60 and 90 mV, respectively, toward the cathode side. Moreover, the photocurrent of the h-FeOOH/Fe₂O₃ anode was slightly higher than that of the d-FeOOH/Fe₂O₃ one. The photocurrent densities of the h-FeOOH/Fe₂O₃ and d-FeOOH/Fe₂O₃ anodes obtained at different FeOOH loading amounts are compared (Fig. S5). The photocurrent densities of both anodes increased and then decreased as the loading amount of FeOOH increased. Owing to the effect of Co-Pi on the catalytic performance of the Fe₂O₃ anode, *V_{on}* decreased by 110 mV. More importantly, when FeOOH and Co-Pi were co-loaded on Fe₂O₃, *V_{on}* could be further reduced. However, the PEC performance of the Co-Pi/h-FeOOH/Fe₂O₃ anode was superior compared to that of the Co-Pi/d-FeOOH/Fe₂O₃ one. For the Co-Pi/h-FeOOH/Fe₂O₃ anode, *V_{on}* was as low as 0.65 V and the photocurrent reached 1.31 mA cm⁻² at 1.23 V, and therefore its *V_{on}* shifted by 270 mV and its photocurrent increased by 54% compared to those of the bare Fe₂O₃ anode. In addition, in the dark, the currents of all electrodes were constant and their values were almost the same. The derived maximum ABPE of Fe₂O₃ was 0.07%, and that increased to 0.10% and 0.12% after d- and h-FeOOH coating, respectively (Fig. S6). The maximum ABPE values of the Co-Pi/Fe₂O₃ and h-FeOOH/Fe₂O₃ anodes were the same but at a smaller applied bias. The maximum ABPE values of the Co-Pi/d-FeOOH/Fe₂O₃ and Co-Pi/h-FeOOH/Fe₂O₃ anodes were 0.13% and 0.20% at 1.0 and 0.94 V, respectively. The IPCE values are in agreement with the measured photocurrents (Fig. 3b). The dual catalyst-loaded photoanodes realized higher IPCE values than the FeOOH or Co-Pi loaded photoanodes. The long-term photocurrents of the Fe₂O₃, h-FeOOH/Fe₂O₃, and Co-Pi/h-FeOOH/Fe₂O₃ photoanodes were measured to investigate their stability (Fig. 3c). While the bare Fe₂O₃ and h-FeOOH/Fe₂O₃ photoanodes exhibited favorable stability after 12 h, the current of the Co-Pi/h-FeOOH/Fe₂O₃ photoanode decreased with time, which indicated that Co-Pi negatively affected the stability of the photoanode. However, the Co 2p XPS profile and the SEM and TEM images of the Co-Pi/h-FeOOH/Fe₂O₃ photoanode presented insignificant changes before and after the long-term stability test (Figs. S7a–c), which confirmed the good adhesion of Co-Pi. The stability of the Co-Pi/Fe₂O₃ photoanode was subsequently evaluated (Fig. S7d), and the decrease in its photocurrent was similar to that of the Co-Pi/h-FeOOH/Fe₂O₃ photoanode. However, during the second run of the stability test, which was performed without turning off/on the light or changing the electrolyte, the photocurrent density of the Co-Pi/Fe₂O₃ photoanode fully recovered and then decreased just as it did during the first run. Similar results have been reported in the literature [35]. Therefore, the decrease in the photocurrent of the Co-Pi/h-FeOOH/Fe₂O₃ photoanode should be attributed to the changes in the properties of the as-deposited Co-Pi during the water oxidation reaction. The Faraday efficiencies of O₂ of all analyzed samples were approximately 90% (Fig. S8). The amounts of H₂ and O₂ gases generated during the first 3 h of the steady-state *I*-*t* test were quantified and the results are pre-

Fig. 2. High-resolution transmission electron micrographs of surfaces of (a) d-FeOOH/Fe₂O₃, (b) h-FeOOH/Fe₂O₃, (c) bare Fe₂O₃, (d) Co-Pi/d-FeOOH/Fe₂O₃ and (e) Co-Pi/h-FeOOH/Fe₂O₃ photoanodes.

Fig. 3. (a) Polarization curves and (b) incident photon-to-current conversion efficiencies (IPCEs) of Fe₂O₃ photoanodes; (c) Steady-state photocurrent test results measured at 1.23 V vs. RHE; (d) Measured amounts of H₂ and O₂ generated by Fe₂O₃, h-FeOOH/Fe₂O₃, and Co-Pi/h-FeOOH/Fe₂O₃ photoanodes at 1.23 V vs. RHE compared to H₂ and O₂ amounts calculated using the generated current.

sented in Fig. 3d. In addition, the H₂/O₂ molar ratio was ~2.03, which was larger than the stoichiometric ratio, and should be attributed to the ineluctable O₂ dissolution at normal pressure and temperature. The H₂ and O₂ evolution analysis demonstrated that the photogenerated carriers mostly participated in the water splitting process in the system. The onset characteristic performance of the Co-Pi/h-FeOOH/Fe₂O₃ photoanode synthesized using this strategy was comparable to those of the previously reported state-of-the-art dual catalyst-modified Fe₂O₃ composite photoanodes summarized in Table S1. The higher photocurrent in the report contributes to Ti doping in Fe₂O₃.

3.3. Photoelectrochemical characterization

The MS plots (C^{-2} vs. V) of the electrodes were obtained in the dark. The slope of the MS plot of the Fe₂O₃ electrode shows a positive (Fig. 4a), which is typical for n-type semiconductors. In addition, the donor concentration of the h-FeOOH/Fe₂O₃ electrode was higher than that of the Fe₂O₃ electrode, which was indistinctive for the d-FeOOH/Fe₂O₃ electrode. The slope of the MS plot of β -FeOOH is negative (Fig. 4b), which confirms its previously reported p-type semiconductor behavior [38]. Thus, β -FeOOH and Fe₂O₃ formed a p-n junction, which explained the higher donor concentration in the FeOOH/Fe₂O₃ electrodes. The UPS-determined valence band positions of β -FeOOH and Fe₂O₃ are determined to be 7.19 and 6.88 eV relative to the vacuum level, respectively (Fig. 4c). The band alignment and formation of the p-n junction between Fe₂O₃ and β -FeOOH were determined using their bandgaps and MS plot-derived flat-band potentials, and the results are presented

in Fig. 4d. Consequently, the transfer of charge carriers was driven by the built-in electric field between β -FeOOH and Fe₂O₃.

The recombination of the photogenerated electrons in Fe₂O₃ photoanodes is schematically illustrated in Fig. 5a. In addition to the recombination of electrons with the holes in the bulk (Step 1, >0.001 s) and in the depletion region (Step 2, 0.01–0.1 s), electrons could be trapped by surface trap states (Step 3, seconds to minutes) [39,40]. The time scale of the normalized transient decay profile of the open-circuit potential (OCP) ranges from 0.01 s to minutes (Fig. 5b), and thus it provides information on the charge recombination in both the depletion region and the surface states (Steps 2 and 3, respectively). Given that the current that resulted from the assumed redox reactions did not pass through, the catalytic and kinetic effects were excluded under the open circuit conditions [41]. As light was switched off, the OCP of bare Fe₂O₃ increases by only 20% within 0.1 s, which indicated that electrons were mostly trapped by the surface states other than being recombined at the surface. For the FeOOH/Fe₂O₃ photoanodes, the decrease in OCP slowed down. The inhibited surface charge recombination that occurred during Step 2 could be explained by the formation of the p-n junction between FeOOH and Fe₂O₃, and the slower Step 3 of h-FeOOH/Fe₂O₃ than that of d-FeOOH/Fe₂O₃ could be caused by the larger electrochemical surface area of h-FeOOH compared to that of d-FeOOH, which hindered charge accumulation. The decrease in the OCP of the Co-Pi-coated anodes was completed within 1 s, which implied that Co-Pi efficiently interfered with the surface states via passivation. During the first second, the OCP of the Co-Pi/d-FeOOH/Fe₂O₃ and Co-Pi/h-FeOOH/Fe₂O₃ anodes decreased faster than those of

Fig. 4. Mott-Schottky (MS) plots of (a) Fe_2O_3 and (b) $\beta\text{-FeOOH}$ photoanodes collected in the dark at the constant frequency of 10 kHz. (c) Ultraviolet photoelectron spectroscopy (UPS) profiles of Fe_2O_3 and $\beta\text{-FeOOH}$ electrodes. (d) Scheme of band alignment and formation of p-n junction between Fe_2O_3 and $\beta\text{-FeOOH}$ derived from MS and UPS data. Here VB and CB denote the valence and conduction bands, respectively, N_d denotes the carrier density, VB_{max} denotes the valence-band maximum, E_v , E_F , and E_{cutoff} denote the vacuum level, Fermi energy and electron cut-off position, and V_{Ac} denotes the vacuum level.

Fig. 5. (a) Recombination of photogenerated electrons in Fe_2O_3 photoanodes. (b) Normalized open circuit potential (OCP) decay diagrams of Fe_2O_3 photoanodes recorded with the light on-off cut. (c) Equilibrium OCP values under dark and illumination conditions. Here E_{CB} and E_{VB} denote the energy levels of the conduction and valence bands, respectively, V_{ph} denotes the photovoltage, V , V_{Light} and V_{Dark} denote the open-circuit voltage, equilibrium open-circuit voltage under light illumination and equilibrium open-circuit voltage in the dark, respectively.

the $\text{d-FeOOH}/\text{Fe}_2\text{O}_3$ and $\text{h-FeOOH}/\text{Fe}_2\text{O}_3$ ones. The enhancement in surface charge recombination partly resulted from the increase in the amount of spatial charges in the depletion region with enlarged band bending [42–44]. The photovoltage (V_{ph}) of the anodes was calculated as the difference between the equilibrium OCP values under illumination and in the dark ($\text{OCP}_{\text{light}}$ and OCP_{dark} , respectively). Owing to the Fermi level pinning effect, OCP_{dark} of the Fe_2O_3 anode equaled the peak position of the surface states and it is determined to be 0.85 V in this study (Fig. 5c) [27,45]. The decrease in the OCP_{dark} values of the two $\text{FeOOH}/\text{Fe}_2\text{O}_3$ anodes revealed that FeOOH shifted the surface states toward a higher position. The OCP_{dark} of the $\text{Co-Pi}/\text{Fe}_2\text{O}_3$ anode was 1.1 V, which implied that the surface states were incompletely passivated. The addition of FeOOH between Co-Pi and Fe_2O_3 in the $\text{Co-Pi}/\text{FeOOH}/\text{Fe}_2\text{O}_3$

anodes induced a decrease in its OCP_{dark} that was similar to that observed for the bare Fe_2O_3 anode. However, the V_{ph} values of the $\text{Co-Pi}/\text{h-FeOOH}/\text{Fe}_2\text{O}_3$ and $\text{Co-Pi}/\text{d-FeOOH}/\text{Fe}_2\text{O}_3$ anodes were higher and lower, respectively, than that of the $\text{Co-Pi}/\text{Fe}_2\text{O}_3$ one. This indicated that the associated amount of photogenerated electron-hole pairs of the $\text{Co-Pi}/\text{h-FeOOH}/\text{Fe}_2\text{O}_3$ anode was higher than that of the $\text{Co-Pi}/\text{Fe}_2\text{O}_3$ one.

PEIS is a powerful tool that could be used to elucidate the kinetics of the photoelectrodes under illumination. The typical Nyquist plots and proposed equivalent circuit used to interpret the PEIS data are presented in Fig. S9. The derived bulk capacitance (C_{bulk}) and resistance (R_{bulk}) as well as the trapping capacitance (C_{trap}) and resistance ($R_{\text{ct,trap}}$) were plotted as functions of the applied potential. The C_{bulk} and $R_{\text{ct,bulk}}$ values (Fig. S10) mostly depended on the bulk Fe_2O_3 , and were insignifi-

Fig. 6. Trapping (a) capacitance (C_{trap}) and (b) resistance ($R_{\text{ct,trap}}$) vs. potential (V) plots of Fe_2O_3 photoanodes under AM 1.5 illumination derived from photoelectrochemical impedance spectroscopy data.

cantly affected by the FeOOH or Co-Pi coatings. However, C_{trap} and $R_{\text{ct,trap}}$ varied significantly (Fig. 6). The C_{trap} plot of the bare Fe_2O_3 electrode presented convex shape and C_{trap} peaked at 1.1 V. In the voltage range of 0.65–0.8 V, the C_{trap} values of d-FeOOH/ Fe_2O_3 were slightly higher than those of bare Fe_2O_3 , whereas the C_{trap} values of h-FeOOH/ Fe_2O_3 increased more significantly. Furthermore, the C_{trap} values at potentials that exceeded 0.8 V were constant for both d-FeOOH/ Fe_2O_3 and h-FeOOH/ Fe_2O_3 . Fe_2O_3 presented both OH- and O-terminated surface states and the potential of the O-terminated surface states was higher than that of the OH-terminated ones [46]. Accordingly, it was concluded that the O-terminated surface states of bare Fe_2O_3 behave dominantly, and FeOOH introduced more OH-terminated surface states. The h-FeOOH nanoparticles induced higher C_{trap} values than the d-FeOOH layer probably owing to h-FeOOH inducing a larger amount of photogenerated holes than d-FeOOH did. The decrease in the C_{trap} values of Co-Pi/ Fe_2O_3 at potentials exceeding 0.9 V reflected the passivated surface states. Furthermore, the C_{trap} of Co-Pi/ Fe_2O_3 peaked at 0.65 V. The co-loading of d-FeOOH and Co-Pi did not affect this peak C_{trap} value; however, the co-loading of h-FeOOH and Co-Pi significantly increased the C_{trap} values, which indicated that the Co-Pi/h-FeOOH/ Fe_2O_3 presented higher hole capture ability than Co-Pi/d-FeOOH/ Fe_2O_3 . The $R_{\text{ct,trap}}$ values of bare Fe_2O_3 decreased as the potential increased and were significantly reduced when FeOOH and Co-Pi were co-loaded on Fe_2O_3 (Fig. 6b). The $R_{\text{ct,trap}}$ values in the potential range of 0.65–0.8 V decreased as follows: bare Fe_2O_3 > d-FeOOH/ Fe_2O_3

> h-FeOOH/ Fe_2O_3 > Co-Pi/d-FeOOH/ Fe_2O_3 > Co-Pi/h-FeOOH/ Fe_2O_3 .

Ponomarev and Peter used charge transfer/recombination processes, and proposed a phenomenological model for estimating the kinetic rate constants [47]. The model had been previously used to estimate the kinetic parameters of the Fe_2O_3 electrode assuming that the capacitance of the semiconductor was much smaller than that across the Helmholtz layer [48,49]. The charge transfer rate (k_{ct}) only depended on the time constant of the surface trapping states, and could be expressed as follows:

$$k_{\text{ct}} = 1/(R_{\text{ct,trap}} \cdot C_{\text{trap}}). \quad (5)$$

The relationship between the charge recombination rate (k_{rec}) and k_{ct} could be written as:

$$k_{\text{rec}} = R_{\text{ct,trap}}/R_{\text{ct,bulk}} \cdot k_{\text{ct}}. \quad (6)$$

The charge transfer efficiency (Φ_{ct}) could be calculated as the charge transfer distribution ratio:

$$\Phi_{\text{ct}} = k_{\text{ct}}/(k_{\text{ct}} + k_{\text{rec}}). \quad (7)$$

The dependence of the calculated kinetic parameters on the potential is depicted in Fig. 7. As the potential increased from 0.5 to 1.1 V, the k_{ct} value of bare Fe_2O_3 increased by two orders of magnitude (Fig. 7a). This dependence of k_{ct} on the applied potential is typical for Fermi level pinning [49,50]. Both d- and h-FeOOH contributed to the increase in k_{ct} . However, d-FeOOH only increased k_{ct} at biases lower than 0.9 V whereas h-FeOOH prompted the permanent increase in k_{ct} at all recorded applied biases. Both d- and h-FeOOH could accelerate the charge transfer kinetics; however, their mechanisms might be different. A

Fig. 7. Plots of (a) charge recombination rate (k_{rec}) and (b) charge transfer rate (k_{ct}) of Fe_2O_3 photoanodes vs. potential (V) determined using photoelectrochemical impedance spectroscopy data; (c) Comparison of measured and estimated photocurrents.

similar increase in k_{ct} was reported for a FeOOH-covered Ti:Fe₂O₃ anode [51]. For the Co-Pi-coated photoanodes, d-FeOOH co-loading led to a significant increase in k_{ct} ; however, the change in k_{ct} associated with the co-loading of h-FeOOH and Co-Pi was negligible. The initial charge recombination rate of bare Fe₂O₃ was higher than its charge transfer rate, which prevented the oxidation of water (Fig. 7b). Both d- and h-FeOOH co-loading led to the slight decrease in k_{rec} with no impact on the variation tendency. The changes in k_{rec} of Co-Pi/Fe₂O₃ were flattened and at potential lower than 0.95 V k_{rec} is reduced. The less dependency of potential is caused by surface states passivation and the reduction in charge recombination at less positive potentials is partly owing to the expanded depletion region (Fig. 5c). The k_{rec} of the Co-Pi/d-FeOOH/Fe₂O₃ photoanode was not significantly different than that of d-FeOOH/Fe₂O₃. By contrast, the k_{rec} of the Co-Pi/h-FeOOH/Fe₂O₃ anode was significantly lower than that of h-FeOOH/Fe₂O₃. Therefore, Co-Pi worked synergistically with d-FeOOH to slightly accelerate the charge transfer, but its combination with h-FeOOH could significantly delay the charge recombination. The calculated Φ_{ct} values and J - V results are compared, as shown in Fig. 7c. The Φ_{ct} values of all samples were consistent with the J - V results, and thus justified the applicability of this model for the photoanodes in this study.

3.4. Dynamics mechanism

The charge transfer and recombination processes for the bare and hybrid Fe₂O₃ photoanodes are schematically illustrated in Scheme 1. The holes photogenerated in Fe₂O₃ transferred from the O-terminated surface state (SS1) participated in the water oxidation reaction (Scheme 1a). The locations of the surface states determined the onset potential [52,53]. Moreover, significant charge recombination occurred at the

surface states and limited the maximum photocurrent. OH-terminated surface states (SS2) were present in the d-FeOOH-loaded Fe₂O₃ photoanode (Scheme 1b), and hole transfer and recombination occurred at both SS1 and SS2. The potential of SS2 was higher than that of SS1, and thus it allowed for a lower onset potential. Furthermore, owing to the formation of the p-n junction for the h-FeOOH/Fe₂O₃ photoanode (Scheme 1c), the transfer of the photogenerated electrons and holes between h-FeOOH and Fe₂O₃, and consequently the bulk recombination, was inhibited, which explained the photocurrent density of h-FeOOH/Fe₂O₃ was slightly higher than that of d-FeOOH/Fe₂O₃. Most surface states of the Co-Pi coated Fe₂O₃ were passivated (Scheme 8d), and therefore the pinned quasi-Fermi level (E_{fp}) was relieved. The remaining surface states were not considered for simplification. Thus, the holes transferred directly from the valence band to Co-Pi and participate in the oxidation of water via several intermediate processes that involved Co⁴⁺ ions [54]. In addition, the electrons in the conduction band recombined with the Co species of Co-Pi, and thus, inhibited the catalytic effect [50]. Upon the co-loading of d-FeOOH and Co-Pi, the amorphous d-FeOOH acted more like a hole-transfer media and an electron-blocking layer, and thus, accelerated the charge transfer to some extent. By contrast, the holes in the valence band of Fe₂O₃ migrated toward β -FeOOH under the force of the electric field of the p-n junction, and eventually transferred to Co-Pi together with those photogenerated in β -FeOOH. Consequently, the amount of accumulated surface electrons was reduced and the charge recombination rate was lowered.

4. Conclusions

In this study, nanostructured Fe₂O₃ was synthesized hydrothermally and used as a benchmark photoanode for PEC water

Scheme 1. Schematics of photogenerated charge transfer pathways at electrode/electrolyte interface. The red and green arrows represent the charge recombination rate (k_{rec}) and hole transfer rate (k_{ct}), respectively. (a) Significant charge recombination occurred at the surface of Fe₂O₃. (b) Surface catalytic effect of d-FeOOH. (c) Charge transfer at p-n junction of β -FeOOH/Fe₂O₃. (d) Catalytic effect of Co-Pi loading. (e) Charge transfer across Co-Pi/d-FeOOH interface. (f) Synergistic effect of β -FeOOH and Co-Pi co-loading. Here SS1 and SS2 denote O- and OH-terminated surface states, respectively, E_{CB} and E_{VB} denote the energy levels of the conduction and valence bands, respectively, and E_{fn} and E_{fp} denote the pinned quasi-Fermi energy levels of the n- and p-types semiconductors.

oxidation. The co-loading of Co-Pi and hydrothermally synthesized h-FeOOH nanoparticles was demonstrated to present synergistic effect on the lowering of the onset potential and enhancement of the photocurrent of the Fe₂O₃ photoanode. By contrast, the synergy between Co-Pi and amorphous FeOOH, which was synthesized via dip-coating, was negligible. The onset potentials of the Co-Pi/h-FeOOH and Co-Pi/d-FeOOH dual catalysts cathodically shifted by 270 and 170 mV, respectively. In addition, the photocurrent density of the Co-Pi/h-FeOOH/Fe₂O₃ anode reached 1.31 mA cm⁻² at 1.23 V vs. RHE; moreover, the onset potential of this anode was as low as 0.65 V vs. RHE, which was comparable to those of the previously reported dual catalyst-modified Fe₂O₃ composite photoanodes. The kinetics of charge transfer and recombination processes were investigated using photoelectrochemical and impedance measurements. When d-FeOOH was added between Co-Pi/Fe₂O₃, the charge transfer was slightly accelerated, but the charge recombination rate was barely affected, which implied that the amorphous d-FeOOH acted as a hole-transfer medium and weakly promoted the charge transfer kinetics. By contrast, the charge recombination of the Co-Pi/h-FeOOH/Fe₂O₃ photoanode was significantly inhibited, which was attributed to the reduced accumulation of surface electrons owing to the formation of the p-n junction between the p-type β-FeOOH and n-type Fe₂O₃ semiconductors. Therefore, the addition of a full-contact layered and granular p-type cocatalyst to photoanode materials could be a suitable strategy to obtain photoanodes with excellent PEC performance.

Supplementary data

Supplementary data associated with this article can be

found in the online version.

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Graphical Abstract

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Functional principle of the synergistic effect of co-loaded Co-Pi and FeOOH on Fe₂O₃ photoanodes for photoelectrochemical water oxidation

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Layered d-FeOOH and granular h-FeOOH play different roles when working synergistically with Co-Pi to reduce the onset potential of Fe₂O₃ photoanodes. A strong synergistic effect is achieved by combining h-FeOOH and Co-Pi.

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Co-Pi与FeOOH对Fe₂O₃光阳极用于光电化学氧化的协同作用原理

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摘要: 利用太阳能光电解水反应制氢为解决能源危机和环境问题提供了一条途径, 是目前研究的热点方向。目前研究较多的一种光阳极材料是 α -Fe₂O₃, 其禁带宽度窄(2.0–2.2 eV), 水稳定性高且天然丰度高。但是, Fe₂O₃的导带位置低于水还原电极电势, 而且Fe₂O₃表面存在大量的表面态, 造成费米能级“钉扎”效应, 使其开启电压高达0.8–1.0 V。大量研究表明, 在Fe₂O₃表面负载水氧化助催化剂可以有效降低其开启电压, 但多数研究集中于采用单一催化剂, 提升效率有限。已有采用双助催化剂提升Fe₂O₃光电效率的研究报道, 但是对其协同作用原理解释不清晰。更重要的是, 双助催化剂的性质选择没有一致性规律, 这给复合型助催化剂的研究带来了不确定性。

本文研究了Co-Pi与FeOOH对Fe₂O₃光阳极的协同作用原理。分别通过浸涂法和水热法制备了两种FeOOH, 在得到的FeOOH/Fe₂O₃光阳极表面通过光电化学方法制备Co-Pi薄膜。采用电化学阻抗谱表征和电化学动力学分析, 重点研究两种FeOOH与Co-Pi形成复合助催化剂对Fe₂O₃光阳极开启电压的协同作用原理及差异, 旨在指导双助催化剂的复合方案。

X射线衍射(XRD)和高分辨透射电镜(HRTEM)表征结果表明, 浸涂法得到的FeOOH为无定形薄膜(记为d-FeOOH), 水热法得到的FeOOH为颗粒状的结晶 β -FeOOH(记为h-FeOOH). 采用X射线光电子能谱(XPS)和扫描电镜(SEM)元素面扫证明了Co-Pi的成功负载. H-FeOOH/Fe₂O₃比d-FeOOH/Fe₂O₃具有更高的电化学活性表面积. 从极化曲线可以看出, Co-Pi/h-FeOOH双助催化剂使Fe₂O₃的开启电压降低了270 mV, 而Co-Pi/d-FeOOH仅能使其降低170 mV, 并且Co-Pi/h-FeOOH/Fe₂O₃的光电流有明显提升. 因此, Co-Pi与h-FeOOH产生了显著的协同作用, 但是与d-FeOOH的协同作用很弱. 莫特-肖特基(Mott-Schottky)和紫外光电子能谱(UPS)证明h-FeOOH与Fe₂O₃之间形成了P-N结, 提升了载流子浓度, 增强了电极导电性. 开路电压(OCP)测试证明了FeOOH负载后Fe₂O₃表面形成了新的表面态, 该表面态位置更负, 因此使Fe₂O₃的开启电压提升. 光电化学阻抗谱(EIS)测试结果表明, Co-Pi和h-FeOOH复合之后表面空穴捕获能力显著提升, 同时伴随着电阻下降, 而Co-Pi和d-FeOOH复合之后对表面电容和电阻的影响不大. 通过动力学分析可知, Co-Pi/h-FeOOH/Fe₂O₃光阳极表面空穴转化速率有所提升, 同时电荷复合速率显著下降.

综上所述, Co-Pi/h-FeOOH的协同效应主要归因于h-FeOOH/Fe₂O₃之间P-N结的形成显著抑制了表面电荷复合, 其次是由于颗粒状的h-FeOOH与Co-Pi之间具有更大的接触表面. 然而, Co-Pi/d-FeOOH/Fe₂O₃阳极中的非晶薄层FeOOH仅作为空穴传输介质, 对电荷转化动力学的促进作用较弱.

关键词: Fe₂O₃; 协同作用; 开启电压; 光阳极; 水分解

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