Hematite photoanode with complex nanoarchitecture providing tunable gradient doping and remarkable low onset potential for advanced PEC water splitting

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Abstract

Over the past years, α -Fe₂O₃ (hematite) has re-emerged as a promising photoanode material in photoelectrochemical (PEC) water splitting. In spite of considerable success in obtaining relatively high solar conversion efficiency, the main drawbacks hindering practical application at hematite are related to an intrinsically hampered charge transport and a sluggish kinetics of the oxygen evolution reaction on the photoelectrode surface.

In the present work, we report a strategy how to synergistically address both these critical limitations. Our approach is based on three key features that are applied simultaneously, specifically i) a careful nanostructuring of hematite photoanode in the form of nanorods, ii) doping of hematite by Sn⁴⁺ ions by a controlled gradient, and iii) surface decoration of hematite by a new class of double hydroxide layered (LDH) OER co-catalysts based on Zn-Co LDH. All three interconnected forms of functionalization result in an extraordinary cathodic shift of the photocurrent onset potential by more than 300 mV and a PEC performance that reaches a photocurrent density of 2.00 mA/cm² at 1.50 V_{RHE}.

Keywords: Zn-Co LDH, Hematite, Gradient doping, PEC water splitting, OER catalyst

Introduction

Photoelectrochemical (PEC) water splitting has received great attention owing to the increasing demand for renewable clean energy which can address the economic and environmental problems deriving from fossil energy.^{[1]-[2]} Semiconductors used in PEC cells split water into oxygen and hydrogen gas by using photoexcited electron-hole pairs (EHP), separated through the formation of the space charge layer (SCL) at the solid/liquid interface.^{[3],[4]} The overall water splitting can be divided into two half reactions, namely, the

oxygen evolution reaction (OER, $2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{O}_2 + 4\text{H}^+$) and the hydrogen evolution reaction (HER, $4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$), occurring at the photoanode and at the photocathode, respectively.^{[5],[6]} Many n-type semiconductors with suitable bandgap energy for absorbing solar light, such as TiO_2 ,^[7] ZnO ,^[8] $\alpha\text{-Fe}_2\text{O}_3$,^[9] BiVO_4 ,^[10] Ta_3N_5 ^[11] and WO_3 ^[12], have been extensively investigated as photoanodes for PEC water splitting. In particular, hematite ($\alpha\text{-Fe}_2\text{O}_3$) is considered a promising photoanode material due to a band gap of 2.1 eV, earth-abundance, simple fabrication processing, enhanced stability against chemical and PEC corrosion, and superior theoretical solar-to-hydrogen (STH) efficiency (15.3 %).^[13–15] However, PEC performance of $\alpha\text{-Fe}_2\text{O}_3$ has been hindered by intrinsic material limitations resulting in a late onset potential (0.9–1.1 V_{RHE}),^[16] short hole-diffusion length ($L_{\text{h}} \approx 2\text{--}4\text{ nm}$),^[17] poor OER property^[18] and high charge recombination rate^{[19][20]}. Reducing the onset potential of $\alpha\text{-Fe}_2\text{O}_3$ photoanodes is one of the most important issues for realization of hydrogen generation through unassisted PEC water splitting. Various strategies, including the use of passivation layers and/or co-catalysts have shown to reduce the onset potential of $\alpha\text{-Fe}_2\text{O}_3$.^{[3],[21]} For instance, various layers containing TiO_2 ,^[22] Al_2O_3 ,^[23] Ti-doped SiO_x ,^[9] Ga_2O_3 ^[24] and amorphous phosphorus,^[25] induced enhanced PEC performance by passivating surface states of $\alpha\text{-Fe}_2\text{O}_3$. Furthermore, diverse co-catalysts including FeOOH ,^[26] IrO_2 ,^[14] $\text{Ni}(\text{OH})_2$,^{[27],[28]} and Co-Pi ^{[29],[30]} have been widely studied for decreasing onset potential by increasing OER property of $\alpha\text{-Fe}_2\text{O}_3$. Overall, the picture resulting from these studies suggest that a complementary contribution from surface state passivation and enhanced surface catalysis is responsible for the observed gain in onset potential for functionalized $\alpha\text{-Fe}_2\text{O}_3$.

The search for efficient electrocatalysts for OER that replace the classic, costly RuO_2 ^[31] and IrO_2 ^[32], has recently stimulated the discovery of novel nanomaterials for OER, such as metal hydroxides (i.e. $\text{Co}(\text{OH})_2$ ^[33] and $\text{Ni}(\text{OH})_2$ ^[34]), metal oxyhydroxides (i.e. FeOOH ,^[35] NiOOH ^[36]

and $\text{CoOOH}^{[37]}$), metal layered double hydroxides (i.e. Zn-Co LDH,^[38] Ni-Co LDH^[39] and Ni-Fe LDH^[40]), an perovskites (i.e. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$,^[41] LaNiO_3 ^[42] and $\text{Na}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.2}\text{Co}_{0.8}\text{O}_3$ ^[43]). These co-catalysts can be coupled to the semiconductor in PEC water splitting, thus providing a further step forward in performance. Among these materials, layered double hydroxides (LDHs) are a class of anionic layered materials consisting of positively charged brucite-like layers balanced by charge anions and solvation molecules placed within the interlayer space.^[44] The diverse combination of cations in LDH layers provides them enhanced catalytic properties when active elements are properly positioned in the structure. Zinc-Cobalt LDHs (Zn-Co LDHs) have been considered a promising OER catalyst because of the excellent catalytic property of cobalt and the high surface area of the two-dimensional morphology.^{[38],[45]}

Here we report a Zn-Co LDH decorated Ti/Sn co-doped $\alpha\text{-Fe}_2\text{O}_3$ nanostructure fabricated through a multistep preparation route including a simple microwave synthesis of Zn-Co LDH, hydrothermal growth of $\alpha\text{-Fe}_2\text{O}_3$ nanorods, and a dip-coating method for the attachment of Zn-Co LDH on the $\alpha\text{-Fe}_2\text{O}_3$ surface. The concentration of Sn^{4+} ions is effective in controlling the width of the SCL and thus reducing recombination, and leading to a decreased onset potential. The Zn-Co LDH nanosheets prepared by a simple one-step microwave-assisted method show superior charge exchange ability between $\alpha\text{-Fe}_2\text{O}_3$ and an alkali electrolyte. The synergistic effect of Zn-Co LDH decoration and gradient Sn^{4+} doping in $\alpha\text{-Fe}_2\text{O}_3$ results in decreasing the onset potential of more than 300 mV, from 0.86 V_{RHE} to 0.54 V_{RHE} , and in increasing photocurrent density from 1.30 mA/cm^2 to 2.00 mA/cm^2 at 1.50 V_{RHE} .

Results and discussion

Figure 1 (a-d) shows the SEM images of 1-time and 2-times grown reference Ti/Sn- Fe_2O_3 (H1 and H2) nanostructures, revealing the typical coral-like or rod shape morphology of $\alpha\text{-Fe}_2\text{O}_3$.

Fe_2O_3 structures synthesized through wet chemical methods.^[27,28,46] The length of rods' major axis in H1 ranges from 45 nm to 425 nm, while in H2 ranges from 55 nm to 575 nm (Figure 1a-1b and S1). The average film thickness of H1 (Figure 1c) and H2 (Figure 1d) is 253 nm and 480 nm, respectively, indicating that 2-times growth process is effective to increase the thickness and rods' length. The different thickness is also confirmed by the higher intensity of (110) plane XRD reflection for H2 than H1 (Figure S2), which also suggests a preferential growth of H1 and H2 along the (110) crystallographic direction, the most conductive and desirable for PEC water splitting.^[47] After a high temperature annealing process (750 °C for 16 min), Ti^{4+} ions from oxidized TiCl_3 , used during the wet chemical synthesis, and Sn^{4+} ions that can diffuse into the lattice of $\alpha\text{-Fe}_2\text{O}_3$ from underneath FTO glass, give rise to a double doped Ti/Sn- Fe_2O_3 structure. To confirm the presence of dopant into $\alpha\text{-Fe}_2\text{O}_3$ lattice, we performed XPS measurements of H1 and H2 samples in the spectral regions of the Ti 2p peak (Figure 1e) and the Sn 3d peak (Figure 1f). The atomic concentration of Ti in H2 (0.95%) is similar, within the experimental sensitivity of the instrument, to the one found in H1 (0.76%), in agreement with synthetic conditions where the same concentration of Ti-dopant in the precursor solution was used^[6,9] (Figure 1e and Table S1). Strikingly, the surface atomic concentration of Sn^{4+} in H2 (1.50 %) is 2.4 times lower than that of the H1 (3.56%). This is attributed to the different thickness of H2 and H1 $\alpha\text{-Fe}_2\text{O}_3$ films. In particular, Sn^{4+} ions are known to diffuse into the lattice of $\alpha\text{-Fe}_2\text{O}_3$ from the FTO glass substrate upon high temperature annealing processes.^[48] Therefore, Sn^{4+} ions reach more easily the surface of 270 nm thick $\alpha\text{-Fe}_2\text{O}_3$ (H1) than that of 480 nm thick sample (H2). The XPS depth profile of H2 and H1 confirms the gradual increase of Sn^{4+} concentration passing from the top to the bottom of film thickness (Figure S3). The metal ions such as Ti^{4+} and Sn^{4+} that are doped inside of $\alpha\text{-Fe}_2\text{O}_3$ may enhance the conductivity of $\alpha\text{-Fe}_2\text{O}_3$ and thus result in an enhanced PEC performance. However, metal ions

located near the surface of α -Fe₂O₃ not only can reduce the width of the SCL but also may become recombination centers due to newly generated energy level in α -Fe₂O₃, and eventually lead to an increased onset potential and decreased photocurrent density.^{[50],[51]} Figure S4 shows the resulting higher photocurrent density and lower onset potential of H2 compared with H1 due to a lower concentration of Sn⁴⁺ ion at surface of H2 and different gradients in Sn⁴⁺. In comparison to H1, the thicker α -Fe₂O₃ nanorods of H2 can generate a greater number of EHPs that can effectively reach the charge collector due to high conductivity resulting from the optimal concentration of Sn⁴⁺ ions at bulk α -Fe₂O₃ region of H2. In addition, the lower concentration of Sn⁴⁺ at the surface of H2 keeps the thickness of the SCL similar to that one of pure α -Fe₂O₃, thus decreasing charge recombination, while reducing the onset potential.^[52] To further increase the PEC performance of our α -Fe₂O₃ photoanodes, the highly efficient OER catalyst Zn-Co LDH has been synthesized and then conformally deposited on α -Fe₂O₃ photoanodes surface by a simple one-pot microwave synthesis and immersion in Zn-Co LDHs suspension, respectively. Briefly, a precursor solution containing zinc nitrate hexahydrate, cobalt nitrate hexahydrate and urea in deionized water and ethylene glycol were placed in microwave oven and treated for 4 min, 10 min, and 18 min with 30s on/off intervals for synthesizing Zn-Co LDH-2, Zn-Co LDH-5, and Zn-Co LDH-9, respectively, as illustrated in the scheme of fabrication (Figure S5).

Figure 2 shows the XRD and XPS spectra of Zn-Co LDHs. The XRD peaks at 2 θ 33.51, 34.93 and 59.16 correspond to (012), (013) and (110) reflections of the brucite-like structure, respectively.^{[45],[53]} The peak at 2 θ 33.51 belongs to the two-dimensional reflection of the turbostratically stacked unit cell.^[54] The XRD pattern of Zn-Co LDH-2 shows several additional peaks related to the presence of Co(OH)₂ and ZnO (Figure 2a) due to short reaction time that hampers the synthesis of LDH sheets. Elemental mapping from EDX analysis during

TEM further confirms this observation, showing that Zn-Co LDH-2 was formed by a ZnO core surrounded by a Co(OH)₂ nanosheet shell (Figure S6). The XPS atomic ratio between Zn and Co, in Zn-Co LDH-2, Zn-Co LDH-5 and Zn-Co LDH-9 was approximately 0.15:1, 1.07:1 and 1.71:1, indicating that the increase in reaction time induces a Zn enrichment in the LDHs surface composition (Table S2). Figure 2b - d display XPS spectra of Zn 2p_{3/2}, Co 2p_{3/2} and C1s of Zn-Co LDHs, respectively. The Zn 2p_{3/2} binding energy of Zn-Co LDH-5 and 9 (1021.98 eV and 1022.08 eV, respectively) is greater than that of the Zn-Co LDH-2 (1021.63 eV), which indicates that Zn²⁺ in Zn-Co LDH-5 and 9 is more polarized by hydroxides than Zn-Co LDH-2.^[55] Considering that Zn-Co LDH-2 majorly consists of Co(OH)₂ sheets, the XPS peak intensity of Zn²⁺ in Zn-Co LHD-2 is lower than those of other LDHs, which is consistent with XRD results. Importantly, XPS atomic ratio of Zn to Co in Zn-Co LDH-5 is 1.07:1, which is very similar to the stoichiometric Zn-Co LDH structure.^[45] In addition, the Co peak of Zn-Co LDHs (Figure 2c) has the same components already reported for other Zn-Co LDH structures as shown in details in Figure S7 for the Co peak deconvolution of LDH-5.^[53] The Co 2p XPS spectrum of Zn-Co LDH-5 is composed of two peaks belonging to Co 2p_{3/2} (781.25 eV) and Co 2p_{1/2} (797.35 eV) with satellite bands at 786.35 eV and 802.95 eV (Figure 2c), respectively. After prolonged microwave exposure, the biding energy of Co 2p_{3/2} and Co 2p_{1/2} of Zn-Co LDH-5 is slightly shifted to lower energy region compared to Co 2p peaks of Zn-Co LDH-2. The peak intensity for satellite bands of Co 2p_{3/2} corresponding to a high-spin Co²⁺ in Zn-Co LDH-5 and 9 is also decreased by partial oxidation of Co²⁺ to Co³⁺.^[56] Since incorporation of Co³⁺ into Zn(OH)₂ forms stable LDH structures, the Zn 2p and Co 2p XPS peaks of Zn-Co LDH-5 and 9 can be evidence for the existence of a LDH phase.^[57] As shown in Table S2, the atomic ratio of the carbon component is increased when the reaction time is increased due to the fast evaporation of precursor solution and carbonization of ethylene glycol

on LDH sheets during the microwave treatment. The high concentration of generated carbons from ethylene glycol increase thickness of Zn-Co LDH-9 cluster by bound each Zn-Co LDH nanosheets (Figure S8).

High-resolution transmission electron microscopy (HRTEM) images and Energy-dispersive X-ray spectroscopy elemental mapping (EDX) of Zn-Co LDH-5 shows that LDH nanosheets are aggregated and composed of O, C, Co and Zn elements (Figure 3a) homogeneously distributed into the material lattice. HRTEM images of Zn-Co LDH-2, 5 and 9 are summarized in Figure S8, highlighting the core-shell morphology of LDH-2 and the nanosheet morphology obtained for both LDH-5 and 9. The magnified TEM image of Zn-Co LDH-5 in Figure 3b demonstrate a lattice spacing of 0.267 nm and 0.256 nm, corresponding to (012) and (013) plane of LDH, respectively, which is consistent with XRD results above. To optimize the attachment condition of Zn-Co LDH on H2 and thus maximizing the semiconductor-cocatalyst interface, H2 photoanodes were immersed in 0.05, 0.1 and 1.0 mg/ml suspensions of Zn-Co LDHs for 10 min followed by washing with water and nitrogen blowing (ZnCo#/H2-0.05, ZnCo#/H2-0.1, ZnCo#/H2-1.0, # = 2, 5, 9). Figure 3c shows the HRTEM image of ZnCo5/H2-0.1 highlighting that Zn-CO LDH nanosheets are highly dense and well-attached on the surface of α -Fe₂O₃ nanorods. Furthermore, it is clear that the 2~4 nm of thin Zn-Co LDH-5 is well distributed on the surface of H2 that has a lattice spacing of 0.25 nm, matching the (110) plane of α -Fe₂O₃ (Figure 3d).

Figure 4a shows the photocurrent density-potential (J-V) curve with chopped light illumination for H1, H2, ZnCo2/H2-0.1, ZnCo5/H2-0.1 and ZnCo9/H2-0.1 in 1M KOH (pH=13.6) under AM 1.5G illumination. The photocurrent density increased from 0.88 to 1.14 mA/cm² at 1.23 V_{RHE} when passing from H1 to H2, while the onset potential shows a 80 mV cathodic shift from 0.86 V_{RHE} (H1) to 0.78 V_{RHE} (H2). The enhanced performance of double-

grown H2 may be due to the Sn^{4+} gradient doping and to an increased light absorption of longer $\alpha\text{-Fe}_2\text{O}_3$ nanorods. After decoration of H2 with Zn-Co LDH, the photocurrent density of ZnCo5/H2-0.1 at 1.50 V_{RHE} reaches 2.00 mA/cm^2 , which is 140% higher than that one of pristine H2 (1.42 mA/cm^2). The synergistic interaction of Zn^{2+} and $\text{Co}^{2+}/\text{Co}^{3+}$ ions in double hydroxide layers of Zn-Co LDH enhances the interaction with water, thus decreasing the OER overpotential of Zn-Co LDH in comparison with $\text{Co}(\text{OH})_2$ or Co_3O_4 .^{[38],[45]} Hence, the photocurrent density of ZnCo5/H2-0.1, which is decorated by Zn-Co LDH nanosheets, is higher than ZnCo2/H2-0.1 that, in contrast, consists of a ZnO core and a $\text{Co}(\text{OH})_2$ nanosheet shell. Interestingly, the photocurrent density of ZnCo9/H2-0.1 containing an excess of Zn^{2+} ions, i.e. Zn:Co ratio 1.71:1, is lower than ZnCo5/H2-0.1 revealing that a precise 1:1 stoichiometry is necessary to achieve LDH with optimized OER activity owing to the poor OER-catalytic properties of Zn^{2+} ions.^{[38],[45]} On the other hand, from the photoanodes obtained after immersion of H2 in Zn-Co LDH suspension at different concentrations, we observe first an increase of PEC performance from 0.05 to 0.1 mg/mL and then a decrease, when using 1 mg/mL LDH suspension (Figure S9). This suggests that the thickness of co-catalyst deposited on the surface of $\alpha\text{-Fe}_2\text{O}_3$ plays a crucial role in enhancing its PEC performance, with a trade-off that has to meet the best thickness/coverage of the hematite surface to passivate surface states, while at the same time providing a well-defined OER catalyst structure to effectively promote OER surface catalysis.^[27] It is noteworthy that the onset potential of H2 is significantly reduced after applying Zn-Co LDH on $\alpha\text{-Fe}_2\text{O}_3$ surface (Figure 4b). The onset potential of H1, H2, ZnCo2/H2-0.1, ZnCo5/H2-0.1 and ZnCo9/H2-0.1 is 0.86, 0.78, 0.58, 0.54 and 0.66 V_{RHE} , respectively. Note the remarkable onset potential difference between H1 and Zn-Co5/H2-0.1 of 320 mV. This cathodic shift of the onset potential is attributed to passivation of surface states and improved catalytic properties of the $\alpha\text{-Fe}_2\text{O}_3$ surface for PEC oxygen formation. The

increased photocurrent density and cathodically shifted onset potential of ZnCo5/H2-0.1 can be explained by synergistic effect of the excellent OER catalytic properties of Zn-Co LDH and a gradient doping with Sn^{4+} where the Sn^{4+} concentration decreases from the bulk to the photoanode surface. Figure 4c shows the incident photon to current efficiencies (IPCEs) of H2, ZnCo2/H2-0.1, ZnCo5/H2-0.1, ZnCo2/H9-0.1 measured at an applied potential of 1.50 V_{RHE} in 1M KOH in the wavelength range from 300 nm to 700 nm. After decoration of the $\alpha\text{-Fe}_2\text{O}_3$ surface with Zn-Co LDH sheets, the IPCE value of $\alpha\text{-Fe}_2\text{O}_3$ over the whole wavelength range (300 – 650 nm) is enhanced. The IPCE at 380 nm is 20.76% for H2 and 28.71% for ZnCo5/H2-0.1. To elucidate the charge transfer mechanism between electrolyte and surface of Zn-Co LDH sheets/ $\alpha\text{-Fe}_2\text{O}_3$, electrochemical impedance spectroscopy (EIS) was carried out in the frequency range from 0.1 Hz to 100 kHz in 1 M KOH at 1.50 V_{RHE} with 369 nm light source (Figure 4d). Nyquist plots for H2, ZnCo2/H2-0.1, ZnCo5/H2-0.1 and ZnCo9/H2-0.1 were fitted by using the equivalent circuit model shown in the inset image of Figure 4d: the resistance between the electrolyte and the semiconductor (R_2) of ZnCo5/H2-0.1 is lower than that of H2, demonstrating a facile charge-transfer from $\alpha\text{-Fe}_2\text{O}_3$ to the electrolyte due to an efficient passivation of $\alpha\text{-Fe}_2\text{O}_3$ surface states by Zn-Co LDH nanosheet layer and due to LDHs excellent OER properties (Figure 4d and Table S3).

Figure 5a shows the stability of the ZnCo5/H2-0.1 and H2 at 1.50 V_{RHE} under AM 1.5G illumination in 1M KOH for 24h. During the stability test, ZnCo5/H2-0.1 shows a steady photocurrent due to the stabilizing effect of alternatively arranged zinc and cobalt ions within the LDH structure. The amount of O_2 and H_2 gas generated in time during PEC water splitting at 1.5 V_{RHE} under AM 1.5G irradiation is displayed in Figure 5b. The measured oxygen and hydrogen gas from ZnCo5/H2 and H2 in time is summarized in Table S4. The theoretical amounts of generated gases has been calculated from the measured current by considering that

two and four electrons are needed to produce hydrogen and oxygen, respectively, for PEC water splitting. The Faradaic efficiency calculated from ratio between measured photocurrent and evolved gas detected with GC measurements is approximately 70% for both H₂ and ZnCo5/H₂-0.1 (Table S5). This shows that a large percentage of photo-generated electron-hole pairs are used to react to O₂/H₂ gas; note that some portion of generated gases is not considered due to gas dissolution and strong adsorption on the electrode surface as reported elsewhere.^[58]

In conclusion, we report a simple strategy for increasing PEC performance of α -Fe₂O₃ photoanode by controlling gradient doping Sn⁴⁺ ions in α -Fe₂O₃ nanorod structure formed through repeated growth and applying Zn-Co layered double hydroxide nanosheets on the α -Fe₂O₃ surface. The optimized Zn-Co LDH/ α -Fe₂O₃ photoanode shows a photocurrent density of 2.0 mA/cm² at 1.50 V_{RHE} and onset potential of 0.54 V_{RHE}, which is cathodically shifted by 320mV from that of a pristine sample. We attribute this enhanced performance to a decreased recombination deriving from the synergistic effect of Sn⁴⁺ gradient doping in the α -Fe₂O₃ nanorod structure and an enhanced OER activity and passivated surface states of the α -Fe₂O₃ resulting from the Zn-Co LDH nanosheet decoration. Our study demonstrates a general strategy that uses gradient doping to decrease charge recombination in the space charge layer, while maintaining high conductivity of hematite photoanodes. In addition, we show that ZnCo double hydroxide is a promising co-catalyst for photoanodes and that its OER activity is strongly dependent on morphology and metal composition.

Experimental Section

Preparation of the reference-1 (H1) and reference-2 (H2) hematite: Hematite photoanodes were synthesized on fluorine-doped tin oxide (TEC-7, FTO) by hydrothermal growth and high temperature annealing process. FTO glasses were cleaned using ultra-sonication with acetone,

ethanol and de-ionized water for 10 min, respectively, and dried by nitrogen-blowing. The cleaned FTO substrates were placed in cap-sealed glass vial with 50 ml of solution containing 150 mM $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 5.5 μl TiCl_3 . The cap-sealed glass vial was placed inside a convection oven at 100 °C for 4 h 30 min for growing β -FeOOH of H1. In the case of H2, the β -FeOOH was grown via 2-time growth process: first, the cleaned FTO glass was placed in convection oven at 100 °C for 1 h with 50 ml solution containing 150 mM $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 5.5 μl TiCl_3 and then washed thoroughly using deionized water; secondly, the grown β -FeOOH was placed in convection oven at 100 °C for 3 h 30 min with same solution for re-growth process. The β -FeOOH on FTO glass was inserted into furnace at 750 °C for 15min to fabricate the final Sn-doped α - Fe_2O_3 .

Preparation of Zn-Co layered double hydroxides (Zn-Co LDHs): To synthesize Zn–Co LDH nanosheets, 44 mg of zinc nitrate hexahydrate (0.15 mmol), 87 mg of cobalt nitrate hexahydrate (0.3 mmol) and 144 mg of urea (2.4 mmol) were dissolved in 10 ml deionized water, and then 40 ml ethylene glycol was added to the above solution. The resulting solution was treated under microwave irradiation in a XH-MC-1 microwave reactor at 750 W for 4 min, 10 min, and 18 min with 30s on/off interval and then cooling naturally for synthesizing Zn-Co LDH 2, Zn-Co LDH 5, and Zn-Co LDH 9, respectively. The product was filtered, washed thoroughly with distilled water and absolute ethanol, and dried at 60 °C overnight.

Preparation of Zn-Co LDH/ α - Fe_2O_3 : The Zn-Co LDH powder was dispersed in deionized water with different density of 0.05 mg/ml, 0.1 mg/ml, and 1 mg/ml, respectively. After Zn-Co LDH solution was sonicated for 10 min, α - Fe_2O_3 electrode (H2) was immersed in 4 ml of Zn-Co LDH solution for 10 min. The Zn-Co LDH/H2 electrodes were washed by deionized water and dried by nitrogen-blowing.

Photoelectrochemical measurement: The photoelectrochemical performance of the hematite photoanodes was measured in a three-electrode PEC cell, where a Pt mesh and Ag/AgCl (3M KCl) electrode acted as counter and reference electrodes, respectively, under illumination of AM1.5G (100 mWcm⁻², 1 sun) in 1M KOH electrolyte. Photocurrent density vs. applied potential (J-V) properties were studied by scanning the potential from -0.5 to 0.8 V at a scan rate of 2 mVs⁻¹. The potentials vs. Ag/AgCl (3M KCl) were converted to the reversible hydrogen electrode (RHE) via the following equation $E_{RHE} = E_{Ag/AgCl} + 0.059pH + E^0_{Ag/AgCl}$, where $E_{Ag/AgCl}$ is the experimentally measured potential, and $E^0_{Ag/AgCl} = 0.209$ V at 25 °C for an Ag/AgCl electrode in 3M KCl. The incident photocurrent conversion efficiencies (IPCE) was acquired in the range from 300 nm to 700nm with 10 nm steps at an applied potential of 1.50 V_{RHE} in 1M KOH. The electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range from 100 kHz to 0.1 Hz at 1.50 V_{RHE} with a perturbation amplitude of 10mV with three-electrode set-up by using a 369 nm L.E.D light source at 0.519 mW/m².

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Figures

Figure 1. Top-view SEM images of (a) H1, and (b) H2. Cross sectional SEM images of (c) H1 and (d) H2. XPS spectra of H1 (red lines) and H2 (black lines) in the Ti 2p (e) and Sn 3d (f) regions.

Figure 2. XRD patterns for Zn-Co LDH-2, Zn-Co LDH-5 and Zn-Co LDH-9 (a). XPS spectra for Zn-Co LDH-2,

Zn-Co LDH-5 and Zn-Co LDH-9 in the regions of (b) Zn 2p and (c) Co 2p.

Figure 3 (a) TEM micrograph (upper) and EDX elemental mapping (bottom) of Zn-Co LDH-5 nanosheets. HRTEM images of (b) Zn-Co LDH-5, and (c-d) Zn-Co LDH-5 decorated α -Fe₂O₃.

Figure 4. J-V curves for samples H1, H2, ZnCo2/H2-0.1, ZnCo5/H2-0.1 and ZnCo9/H2-0.1 measured in the potential range from 0.55 to 1.8 V_{RHE} (a) and a zoom of the region from 0.50 to 1.0 V_{RHE} (b). (c) IPCE spectra of H2, ZnCo2/H2-0.1, ZnCo5/H2-0.1, ZnCo9/H2-0.1 measured at 1.5 V_{RHE}. (d) EIS analysis of H2, ZnCo2/H2-0.1, ZnCo5/H2-0.1, ZnCo9/H2-0.1 at 1.50 V_{RHE} under 369 nm LED source.

Figure 5. (a) Chronoamperometry showing the stability of ZnCo5/H2-0.1 and H2 for 24h at 1.50 V_{RHE} under 1 sun in 1M KOH. (b) Evolution of oxygen and hydrogen gas from ZnCo5/H2-0.1 and H2 (left y-axis) and calculation of faradaic efficiency (right y-axis).

Figure 6. Top-view SEM images of (a) H1, and (b) H2. Cross sectional SEM images of (c) H1 and (d) H2. XPS spectra of H1 (red lines) and H2 (black lines) in the Ti 2p (e) and Sn 3d (f) regions.

Figure 7. XRD patterns for Zn-Co LDH-2, Zn-Co LDH-5 and Zn-Co LDH-9 (a). XPS spectra for Zn-Co LDH-2, Zn-Co LDH-5 and Zn-Co LDH-9 in the regions of (b) Zn 2p and (c) Co 2p.

Figure 8 (a) TEM micrograph (upper) and EDX elemental mapping (bottom) of Zn-Co LDH-5 nanosheets. HRTEM images of (b) Zn-Co LDH-5, and (c-d) Zn-Co LDH-5 decorated α -Fe₂O₃.

Figure 9. J-V curves for samples H1, H2, ZnCo2/H2-0.1, ZnCo5/H2-0.1 and ZnCo9/H2-0.1 measured in the potential range from 0.55 to 1.8 V_{RHE} (a) and a zoom of the region from 0.50 to 1.0 V_{RHE} (b). (c) IPCE spectra of H2, ZnCo2/H2-0.1, ZnCo5/H2-0.1, ZnCo9/H2-0.1 measured at 1.5 V_{RHE}. (d) EIS analysis of H2, ZnCo2/H2-0.1, ZnCo5/H2-0.1, ZnCo9/H2-0.1 at 1.50 V_{RHE} under 369 nm LED source.

Figure 10. (a) Chronoamperometry showing the stability of ZnCo5/H2-0.1 and H2 for 24h at 1.50 V_{RHE} under 1 sun in 1M KOH. (b) Evolution of oxygen and hydrogen gas from ZnCo5/H2-0.1 and H2 (left y-axis) and calculation of faradaic efficiency (right y-axis).

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