FeO-Based Hierarchical Structures on FTO Substrates and Their Photocurrent

Weiwei Xia,* Jiawei Sun, Xianghua Zeng,* Pengdi Wang, Min Luo, Jing Dong, and Huaguang Yu

ABSTRACT: As one of the most promising photoanode materials for photoelectrochemical (PEC) water oxidation, earth-abundant hematite has been severely restricted by its poor electrical conductivity, poor charge separation, and sluggish oxygen evolution reaction kinetics. FeO has an ability to produce hydrogen, while its preparation needs high temperature to reduce Fe³⁺ to Fe²⁺ by using H₂ or CO gases. Here, Fe₂O₃- and FeO-based nanorods (NRs) on fluorine-doped tin oxide (FTO) substrate have been prepared, where the latter was obtained by doping Sn⁴⁺ ions in FeOOH to reduce Fe³⁺ ions to Fe²⁺. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements indicate that the dominant content of Fe element on the surface of Sn-doped Fe₂O₃ and Sn-FeOOH samples is Fe²⁺. FeO-based NRs have a Fe₃O₂/FeO heterostructure with some SnO₂ nanoparticles distributed on their surface. These prepared samples were used as PEC photoanodes under a visible-light irradiation. The results showed that the modified FeO-based NRs have a photocurrent density of 0.2 mA cm⁻² at 1.23 V vs reference hydrogen electrode (RHE) using Hg/HgO electrode as the reference electrode. Furthermore, they also have a better photocatalytic hydrogen evolution activity with a rate of 2.3 μmol h⁻¹ cm⁻². The improved photocurrent and photocatalytic activity can be ascribed to the Sn-dopant, as the introduction of Sn⁴⁺ not only leads to the formation of the Fe₃O₂/FeO heterostructure but also increases the carrier concentration. Fe₃O₂/FeO heterostructure with SnO₂ nanoparticles on its surface has a good band energy alignment, which is beneficial to the PEC water oxidation and reduction.

INTRODUCTION

With stability in aqueous solution, favorable band gap (2.1 eV), and vast abundance, hematite (α-Fe₂O₃) is regarded as one of the most promising photoanode materials for photoelectrochemical (PEC) water oxidation.¹–³ Due to its poor electrical conductivity, poor charge separation and transfer efficiency, and sluggish oxygen evolution reaction (OER) kinetics, the performance of the hematite photoanode for water oxidation needs to be furthermore improved. Element doping⁴–⁷ in hematite (α-Fe₂O₃) was regarded as an efficient method to improve water photo-oxidation. Sn⁴⁺ is a tetravalent dopant that can be substitutionally doped into hematite at the Fe³⁺ sites,⁸–¹⁰ and the electrical conductivity of Sn-doped hematite can be enhanced by the occurrence of bivalent ions, Fe²⁺, where the local pairs of Fe²⁺–Sn⁴⁺ play the role of donor centers in hematite, causing enhanced electro-conductivity,¹¹ and at the same time, retarding the electron–hole recombination.¹² Gonçalves et al.¹³ prepared hematite thin films with high PEC performance of 2.7 mA cm⁻² at 1.23 V_RHE by using the colloidal nanocrystal deposition process, while the samples were sintered over 800 °C. Tang et al.¹⁴ have constructed Fe₂O₃ related multilayer nanowires to enhance PEC water splitting by tuning the surface state. Ma et al.¹⁵ adopted low-temperature hydrogen annealing combined with high-temperature quenching in air to realize self-diffused Sn doping in α-Fe₂O₃ nanorod (NR) photoanodes, where photocurrent densities of 1.35 mA cm⁻² at 1.23 V vs reference hydrogen electrode (RHE) and 1.91 mA cm⁻² at 1.4 V vs RHE were obtained. Li et al.¹⁶ shed light on the improvement of carrier conductivity by combing orientation control and transition metal doping by a magnetic field method. Zhang et al.¹⁷ fabricated Sn-doped hematite films via mid-situ and ex

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situ doping methods to improve PEC performances, where the Sn-doped hematite films on the fluorine-doped tin oxide (FTO) substrate were synthesized by soaking the FeOOH film in the tin salt aqueous solution followed by thermal treatment. Guo et al. obtained a photocurrent of 5.7 mA cm\(^{-2}\) at 1.23 V vs RHE. By changing temperatures and atmospheres, Wang et al. studied the electrical and thermomechanical properties of undoped and Sn-doped \(\alpha\)-Fe\(_2\)O\(_3\) nanoscale powders to investigate their transport and defect properties. Rani et al. studied the different Sn-doped \(\alpha\)-Fe\(_2\)O\(_3\) (Sn = 0, 10, 20, 30 wt %) photoanodes to improve properties of PEC water splitting. Grave et al. studied the orientation dependence of the PEC properties on Sn-doped hematite photoanodes and found that the Sn-doped hematite thin films with (100) and (110) oriented samples can improve the onset potentials of \(\sim 170\) and \(\sim 100\) mV. Li et al. studied morphology and doping engineering of Sn-doped hematite nanowire photoanodes, and an outstanding photocurrent density of 2.2 mA cm\(^{-2}\) at 0.23 V vs Ag/AgCl was obtained. In their studies, the prepared samples need 800 °C for annealing treatment, as the high-temperature thermal annealing will lead to the shrinkage of NWs and the Sn diffusion from the FTO substrate, which yields a nonuniform distribution of Sn doping along the hematite NW growth axis. Therefore, they used a silica encapsulation method to retain the morphology of hematite NWs with a uniform Sn-dopant distribution along the nanowire growth axis.

Although there are many discussions on Sn-doped \(\alpha\)-Fe\(_2\)O\(_3\) photoanodes to improve properties of PEC water splitting, the photocurrent is significantly lower than the theoretical limit of 12.6 mA cm\(^{-2}\) predicted from its band gap energy. The main reasons for the limited performance of hematite photoanodes have been attributed to short lifetime, electrical properties, and significant charge recombination. Furthermore, a facile method needing no high temperature is more welcome. Another iron oxide is wüstite (FeO), which has been used to produce hydrogen in high-temperature solar chemistry. Most studies on FeO were concentrated on the water chemisorption and reaction. As the bulk phase of FeO at room temperature was reported to be thermodynamically unstable, the reported FeO materials were obtained by reducing hematite in hydrogen or carbon monoxide atmospheres under high temperature. It is a fascinating way to prepare wüstite material by a green method.

As wüstite has a conduction band energy of 4.33 eV (vs vacuum energy), wüstite photocatalyst on hydrogen production under visible-light irradiation is a very interesting topic for discussion.

To study the photocurrent of undoped Fe\(_2\)O\(_3\) and Sn-doped FeO, we prepared three samples: undoped Fe\(_2\)O\(_3\), Sn-doped Fe\(_2\)O\(_3\), and Sn-FeOOH NR arrays on the FTO substrate. First, the FeOOH NRs on the FTO substrate were prepared, FeOOH NRs were annealed at 550 °C for 2 h to obtain undoped Fe\(_2\)O\(_3\), and then the Fe\(_2\)O\(_3\) NRs were immersed in the Sn-precursor for 24 h at room temperature and finally sintered at 550 °C for 2 h in a muffle furnace under atmosphere; thus, the Sn-doped Fe\(_2\)O\(_3\) NR arrays were obtained. When FeOOH NRs were directly immersed in the Sn-precursor without the annealing treatment, with the same steps, the Sn-FeOOH NRs were obtained. X-ray photoelectron spectra (XPS) indicate that the dominant state of Fe in sample Sn-doped and Sn-FeOOH NRs is Fe\(^{2+}\), while in undoped Fe\(_2\)O\(_3\), the main state of Fe is Fe\(^{3+}\). At the same time, the prepared samples were used as PEC photoanodes under visible-light irradiation. The results show that sample Sn-FeOOH has a photocurrent density of \(\sim 40.7\) \(\mu\)A cm\(^{-2}\) which is nearly 4-fold of 10.7 \(\mu\)A cm\(^{-2}\) for Sn-Fe\(_2\)O\(_3\), and nearly 24-fold of undoped Fe\(_2\)O\(_3\) NRs (1.7 \(\mu\)A cm\(^{-2}\)). The Sn-FeOOH sample has also a better photocatalytic hydrogen evolution activity with a rate of 2.3 \(\mu\)mol h\(^{-1}\) cm\(^{-2}\).

## RESULTS AND DISCUSSION

The fabrication procedures of Sn-Fe\(_2\)O\(_3\) and Sn-FeOOH are illustrated in Figure 1a. Initially, for Sn-FeOOH, the synthesis process can be separated into two parts: first, a thin film of FeOOH NR arrays is assembled on the FTO substrate; second, the FTO glass substrate coated with FeOOH was immersed in Sn-precursor and sintered at 550 °C under atmosphere. In contrast, Sn-Fe\(_2\)O\(_3\) undergoes an annealing procedure of FeOOH NR arrays on the FTO substrate before immersion of the Sn-precursor. Finally, the Fe\(_2\)O\(_3\) NR arrays coated with Sn-precursor are sintered at 550 °C under atmosphere. Unintentionally, Sn-doped- and SnO\(_2\) nanoparticle-packed Fe\(_2\)O\(_3\)/FeO hierarchical NR arrays were obtained. Figure S1 is the photograph of the obtained Fe\(_2\)O\(_3\), Sn-Fe\(_2\)O\(_3\), and Sn-FeOOH NR arrays; we can observe that the surface of the entire FTO glass substrates is uniformly covered with the red thin film.

To determine the crystal structure of the synthesized samples, XRD measurement was carried out and the result is presented in Figure 1b. Figure 1b shows the XRD patterns of Fe\(_2\)O\(_3\), Sn-Fe\(_2\)O\(_3\), and Sn-FeOOH samples. After subtracting the diffraction peaks originating from the FTO substrate, the extra peaks located at 2θ values 35.61 and 63.99° can be ascribed to the (110) and (300) crystal plane of Fe\(_2\)O\(_3\) (JCPDS card number 33-0664). Apart from the peaks from
Fe$_2$O$_3$ and the FTO substrate, no other diffraction peaks are found from these annealed-treated samples. Specifically, both patterns only show a strong (110) peak and a weak (300) peak, indicating that the growth axis of these hematite NR arrays are highly oriented along the [110] direction vertical to the FTO substrate. Significantly, it has been reported that hematite has a strong anisotropic conductivity, which has 4 orders of magnitude higher along the [110] direction than the orthogonal direction.\textsuperscript{34,35} XRD patterns show that the peaks of the Sn-doped samples are identical to those of the undoped Fe$_2$O$_3$. The peak of the FeO content is not obvious, as its peak overlaps with that of FTO.

Figure 2. Plan view and cross-sectional SEM images of Fe$_2$O$_3$, Sn-Fe$_2$O$_3$, and Sn-FeOOH NR arrays grown on the FTO substrate. (a) and (d) for Fe$_2$O$_3$; (b) and (e) for Sn-Fe$_2$O$_3$; and (c) and (f) for Sn-FeOOH.

The structure and morphology of synthesized NR arrays were further revealed by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). According to the plan view and cross-sectional SEM images, oriented and bundled Fe$_2$O$_3$ NR arrays (about 100 nm in diameter) were synthesized on the FTO substrate (Figure 2a,d). In comparison to the pure Fe$_2$O$_3$ NR arrays, Sn-Fe$_2$O$_3$ and Sn-FeOOH NR arrays sintered at 550 °C under atmosphere faithfully inherit perpendicularly oriented NRs on FTO. It can also be seen that the surface of the entire Sn-Fe$_2$O$_3$ and Sn-FeOOH NRs was covered with a small number of nanoparticles. The higher magnification image (Figure 2c) indicates that the NRs of Sn-FeOOH have a rougher surface with some pores.

TEM measurements were used to further investigate the microstructure of the Sn-Fe$_2$O$_3$ and Sn-FeOOH NRs. To identify each crystal phase via HRTEM and probe the spatial distribution of these components in the obtained NRs, we created crystal models based on the single-crystal date in the Inorganic Crystal Structure Database (ICSD), as displayed in Figure S2. Figure 3a shows a low-magnification TEM image of the Sn-Fe$_2$O$_3$ NRs extracted from the NR arrays on the FTO substrate, which also clearly shows that the surface of Sn-Fe$_2$O$_3$ NRs was covered with a small number of nanoparticles. HRTEM images of two selected segments of a single Sn-Fe$_2$O$_3$ NR are displayed in Figure 3b,c. As shown in Figure 3b, the measured d spacings of 3.34 and 2.64 Å correspond to the (110) and (101) crystal planes of SnO$_2$ (JCPDS card no. 41-1445), respectively. The HRTEM and atomic structure detail of the edge region of an individual NR in Figure 3c demonstrate that the NR is composed of an apparent contrast between the inner core and the outer shell. Besides, the presence of continuous lattice fringes throughout the structure confirms the existence of lattice planes and good crystallinity. Figure 3c reveals a layer of shell about 2–5 nm thick wrapping the surface of the NR. The crystal grain on the edge of the outer shell has an interplanar spacing of 2.60 Å, which corresponds to the d-spacing of (002) planes of FeO (JCPDS card no. 49-1447) consistent with the XRD results. Moreover, the inner core corresponds to the hexagonal Fe$_2$O$_3$, [R-3c]-space group 167, also known as hematite, with lattice...
Fe2O3, Sn-Fe2O3, Sn-FeOOH NR arrays, as shown in Figure 4a. The presence of Sn, O, and Fe elements on the surface of Sn-Fe2O3 and Sn-FeOOH NR arrays, while no Sn element is observed for sample Fe2O3. Peaks located at ~710 and ~723 eV can be assigned to Fe 2p3/2 and 2p1/2 respectively (in Figure 4d). For sample Fe2O3, peaks at a low energy ~710 eV and a high energy 723.8 eV with satellites at 717.8, 731.8, and 741.8 eV could be evidenced as to Fe3+ 2p3/2 and 2p1/2 from Fe2O3. As shown in Figure S4, the peak at ~710 eV can be deconvoluted to be 711.4 and 710.6 eV, and a lower one can be regarded as the content of Fe2+ in Fe2O3 NRs.37 Two typical peaks of Fe3+ at 717.8 and 731.8 eV and the absence of the Fe2+ satellite peak at around 716 eV indicate that the main state of Fe is Fe3+.

For Sn-Fe2O3 and Sn-FeOOH samples, a strong peak at 715.2 eV is the Fe2+ satellite peak. The absence of two peaks at ~718 and ~733 eV indicates39 that the main state of Fe is Fe3+, as shown in Figure 4d. The doping tetravalent ions, Sn4+, can induce the reduction of Fe3+ to Fe2+, as the individual doping tetravalent ion Sn4+ needs an extra electron in comparison to Fe3+; in this way, Fe3+ ion becomes Fe2+. The increased Fe2+ content implies that more Sn4+ ions were doped in the samples.39 As the intensity of the peak located at 715.2 eV for Sn-FeOOH is larger than that of Sn-Fe2O3, it implies more doped Sn4+ ions in Sn-FeOOH. The peak at ~710 eV for the Sn-FeOOH sample can be deconvoluted to be 709.9 and 710.9 eV (shown in Figure S4b), the latter one implies the existence of Fe3+. This phenomenon is consistent with the reported in ref 11, 40, 41. At the same time, the Sn-dopant will shift the binding energy of O 1s spectrum. From the XPS of O 1s spectra (Figure 4f), the peak at 530 eV can be deconvoluted to two peaks at ~529 and ~530 eV (inset of the Figure 4f), the lower energy can be assigned to Fe–O/Sn–O species, and the one at a higher binding energy of ~530.8 eV is ascribed to surface oxygen. We find that the Sn-FeOOH sample has the highest oxygen vacancy, while Sn-Fe2O3 has the lowest one, as listed in Table S1, where the deconvoluted O 1s spectra of the prepared samples are displayed. XPS spectra of Sn 3d are displayed in Figure 4e, where the binding energies range from 485.6 to 494.0 eV for Sn with Sn-FeOOH assigned to Sn 3d5/2 and 3d3/2 respectively. For Sn-FeOOH, the corresponding binding energy has a 0.2 eV blue shift with respect to Sn-Fe2O3, that is, binding energies at 485.8 and 494.2 eV to Sn 3d5/2 and 3d3/2 respectively. The change may be caused by different Sn-doping content.
To further study the charge-transfer process occurring at the interface of the photoelectrode/electrolyte, electrochemical impedance spectroscopy (EIS) was carried out and presented in Figure 5a. As shown in Figure 5a, each Nyquist plot is composed of one semicircle and a slope line; the diameter of the semicircle at high frequencies represents the charge-transfer resistance ($R_{ct}$), which reflects the electron transfer kinetics of the redox probe at the interface. The slope line at low frequency is related to the diffusion process. The smaller the slope, the lower the resistance. Comparing the three samples, Sn-FeOOH has the lowest resistance and Fe$_2$O$_3$ has the largest one. The minimum interfacial resistance of Sn-FeOOH NRs indicates that there are more Fe$^{2+}$ and Sn$^{3+}$ ions in Sn-doped FeO samples, which will be helpful to the photoelectron transferring from FeO to the FTO substrate along the vertically oriented FTO NRs.

Besides the smaller interfacial resistance, Sn-FeOOH NRs exhibited a larger electrochemical specific surface area (Figure 5b) due to more SnO$_2$ nanoparticles on their surface. The PEC measurements were carried out in a three-electrode configuration in 0.1 M Na$_2$SO$_4$ using Pt wire as a counter electrode, Ag/AgCl in saturated KCl as a reference electrode, and the Fe$_2$O$_3$, Sn-Fe$_2$O$_3$, and Sn-FeOOH NRs on FTO substrates as active photoanodes. The incident radiation is switched with an on/off interval of 20 s, and 15 repeated cycles are displayed in Figure 5c, where Fe$_2$O$_3$ NRs display a quite weak photocurrent of 1.7 $\mu$A cm$^{-2}$ under visible-light irradiation; Sn-FeOOH sample exhibits a much-enhanced photocurrent density of $\sim$40.7 $\mu$A cm$^{-2}$, which is nearly 4-fold of Sn-Fe$_2$O$_3$ (10.7 $\mu$A cm$^{-2}$). The photocurrent is stable, as there is only a 10% decrease after 15 cycles.

The transient photocurrent decay was investigated by studying the photocurrent rise and decline. When the light was switched on, the electrodes presented a photocurrent spike and exponentially decayed rapidly to a steady state due to the quick recombination of photogenerated carriers. The transient decay time can be calculated from a logarithmic plot of parameter $D$ based on the following formula

$$D = (I_t - I_m)/(I_m - I_s)$$

where $I_t$ is the current at time $t$ and $I_m$ and $I_s$ are the current spike and stabilized current, respectively. From Figure 5d,e, the transient decay time $\tau$ defined as the time at which $\ln D = -1$ was obtained, is 0.50, 0.28, and 0.41 s for samples Fe$_2$O$_3$, Sn-Fe$_2$O$_3$, and Sn-FeOOH NRs, respectively. Longer $\tau$ means a lower rate of carrier recombination and enhanced charge transfer. 

Figure 5. (a) Nyquist plots of as-prepared samples; (b) capacitive $J$ versus scan rate for samples; (c) photocurrent responses under on/off 20 s for 15 cycles at 0.0 V versus Ag/AgCl with illumination of 300 W Xe lamp; (d) enlarged rising and decaying edges of the photocurrent responses; (e) transient decay times of the obtained samples measured at the same condition; and (f) Linear sweep voltammetry (LSVs) versus Hg/HgO in saturated KOH for FTO, Sn-Fe$_2$O$_3$, and Sn-FeOOH photoanodes collected in the dark and under irradiation of the 300 W Xe lamp.

Figure 6. (a) Photocatalytic H$_2$ evolution from the aqueous solutions as a function of time under irradiation of the 100 W Xe lamp and (b) proposed energy band alignment of the Fe$_2$O$_3$, FeO, and SnO$_2$ electrodes.
separation. Photogenerated e-p carriers were more likely to recombine for sample Sn-Fe2O3. Figure Sf displays the linear sweep voltammetry curves of the bare FTO, Sn-Fe2O3, and Sn-FeOOH NRs observed under dark and light (simulated sunlight) conditions versus Hg/HgO in saturated KOH. Sn-FeOOH photoanode exhibited a better PEC property under visible illumination. The photocurrent of Sn-FeOOH reaches 0.2 mA cm\(^{-2}\) (1.23 V vs RHE). The result is larger than the value obtained with the sample 30% Sn-α-Fe2O3, but lower than the sample 10% Sn-α-Fe2O3 by Rani et al.\(^{20}\) From cyclic voltammetry (CV) of the three samples at various scan rates, the area surrounded with the CV curve of sample Sn-FeOOH is obviously larger than those of the other two samples, indicating better capacitance of that sample, as shown in Figure S5d–f.

Furthermore, the photocatalytic property of the undoped Fe2O3 and Sn-FeOOH NR samples has been studied under visible light, where the evolution of hydrogen was measured according to the photocatalytic water-splitting process, as shown in Figure 6a. The results show that Fe2O3 NRs have almost no photocatalytic hydrogen evolution activity, while the Sn-FeOOH NRs have a rate of 2.3 \(\mu\)mol h\(^{-1}\), which was never reported. As the conduction band potential of Fe2O3 lies below the H2 evolution potential, it is not high enough to drive water reduction without bias.\(^{16}\) As the conduction band potential of FeO (\(-4.33 \text{ V vs vacuum}\)) is above the potential of H\(^+\)/H\(_2\) (\(-4.44 \text{ V vs vacuum}\)), the hydrogen evolution activity can be observed in the presence of large amounts of FeO in the Sn-FeOOH NRs.

**Mechanism.** Mott–Schottky (MS) plots were obtained from the electrochemical impedance spectroscopy measurement for samples Fe2O3, Sn-Fe2O3, and Sn-FeOOH NRs, as shown in Figure S5. From MS curves, the capacitance of the space charge region, formed at the semiconductor/electrolyte interface, is measured to determine the active concentration of dopants. The MS equation is described by

\[
\frac{1}{C^2} = \frac{2}{n_e e \varepsilon_0} \left( V - V_{FB} \right) - \frac{kT}{e} 
\]

where \(k\), \(n_e\), \(\varepsilon\), and \(e\) are the Boltzmann constant, the hole carrier density, the space charge capacitance in the semiconductor, and the elemental charge value, respectively. \(e\) and \(\varepsilon_0\) are the relative permittivity of the semiconductor (\(e = 80\) for hematite\(^{44}\) and 27 for Fe2O3\(^{55}\)) and the permittivity of the vacuum, respectively. \(V\) and \(T\) are the applied potential and temperature, respectively. The slope of the linear part of the curve in the Mott–Schottky plot is positive from \(-0.3\) to \(0.4\) V, indicating an n-type semiconductor induced by oxygen vacancy, and the electron carrier density \(n_e\) can be calculated from the following relation

\[
(n_e) = \frac{2}{\varepsilon e \varepsilon_0 \times \text{slope}} 
\]

From Figure S5bc, the slope was obtained as 12.89 \(\times\) 10\(^3\), 39.77 \(\times\) 10\(^3\), and 29.55 \(\times\) 10\(^3\) cm\(^2\)/F for Fe2O3, Sn-Fe2O3, and Sn-FeOOH NRs, respectively. Then, the respective carrier concentrations are estimated to be 1.37 \(\times\) 10\(^20\), 1.31 \(\times\) 10\(^20\), and 1.77 \(\times\) 10\(^20\) cm\(^{-3}\). Comparing the three samples, the Sn-FeOOH sample has larger carrier density \(n_e\). The improved electrical conductivity and unit cell volume with the increase in the doping concentration of the phase pure powders might be related to the increased Fe\(^{2+}\) state.\(^{46}\)

In PEC cell, as an n-type semiconductor, electrons from the n-type Sn-FeOOH NRs reduce water to form H2 and OH\(^-\) ions, and a positive center will be formed at the interfacial surface of the Sn-FeOOH NRs, resulting in the formation of the built-in electric field, which works in Schottky barrier mode. As the incident photon energy exceeds the band gap energy of FeO (2.4 eV), electron–hole pairs will be generated under visible-light radiation. The generated holes are driven from the valence band of FeO into the interface of SnO2/ electrolyte and captured by the reduced form of the redox molecule (\(h^+ + OH^- \rightarrow OH^+\)), and the hydroxyl radicals OH* are then reduced to OH\(^-\) anions (\(e^- + OH^+ \rightarrow OH^-\)) at the counter electrode. The photogenerated electrons from the conduction band of FeO will transfer to the conduction band of SnO2, which will retard the electron–hole recombination. In this way, more photogenerated electrons from SnO2 can be collected at the FTO substrate and transferred to the working electrode (Pt/FTO) by the external circuit. The circuit was completed in this manner, demonstrating self-powered UV detection.

For sample Sn-Fe2O3, the SnO2 nanoparticles are sparsely distributed on its surface, so the photogenerated electrons from the valence band to the conduction band of FeO will quickly recombine with the hole in the valence band where there are no SnO2 nanoparticles; this is consistent with the result of the shorter transient decay time \(\tau\) in Sn-FeO3 NRs. For the FeO sample, as indicated in the XPS spectra, the dominant content of Fe is Fe\(^{3+}\) with less content of Fe\(^{2+}\). Due to the conduction band energy of FeO being lower than the H2 evolution potential, water reduction could not occur without additional bias, and hence the photocurrent is very low (as shown in Figure 5c).

**CONCLUSIONS**

SnO2 NRs were prepared first by a modified hydrothermal method, then annealed at 550 °C for 2 h with different steps, finally, the Sn-Fe2O3 and Sn-FeOOH NRs on FTO substrates were obtained. In addition to the FeO, Fe2O3 heterostructures in two samples, SnO2 particles with a thickness of tens nm covered on the surface of Sn-FeOOH NRs. Due to a large amount of Sn\(^{4+}\)-doped ions in FeOOH NRs, more and more Fe\(^{3+}\) ions reduced to Fe\(^{2+}\), resulting in the dominant content of Fe ions being Fe\(^{2+}\) in Sn-FeOOH samples. When the prepared samples were used as active photoanodes, Sn-FeOOH NRs exhibit a much-enhanced photocurrent density of \(-40.7 \mu\text{A cm}^{-2}\) in the visible-light spectral region, which is nearly 4-fold of 10.7 \(\mu\text{A cm}^{-2}\) for Sn-FeO3 at 0.0 V versus Ag/AgCl. Using Hg/HgO electrode as a reference electrode, Sn-FeOOH NRs have a photocurrent of 0.2 \(\mu\text{A cm}^{-2}\) at 1.23 V vs RHE, quite larger than that of Sn-FeO3 NRs. Furthermore, the sample has a better photocatalytic hydrogen evolution activity with a rate of 2.3 \(\mu\text{mol h}^{-1}\).

In comparison with the high-temperature reduction of Fe\(^{3+}\) to Fe\(^{2+}\) by using H2 or CO gases,\(^{47}\) here the FeO-based hierarchal structure was obtained by doping Sn\(^{4+}\) ions to reduce Fe\(^{3+}\) ions to Fe\(^{2+}\). Although some studies on hydrogen production by using FeO have been reported, those works are mainly concentrated on high-temperature solar chemistry with a temperature up to 750 °C.\(^{48}\) There are few reports on the photocatalytic hydrogen. Our studies open a new routine to the preparation and to the photocatalytic application of the wüstite (FeO) nanostructures.
**EXPERIMENTAL SECTION**

**Materials.** All chemicals were of analytical grade and used without further purification. Iron (III) chloride hexahydrate (FeCl₃·6H₂O), tin dichloride dehydrate (SnCl₂·2H₂O), acetic acid, ethanol, and hydrochloric acid (HCl, 36.5–38% by weight) were purchased from Sinopharm Chemical Reagent Co., Ltd. Fluorine-doped tin oxide (SnO₂:F, FTO) conducting glass was provided by Hefei Kejing Material Technology Co., Ltd.

**Preparation of Fe₂O₃ NR Array.** FeOOH NR arrays were obtained, labeled as samples Sn-Fe₂O₃ and Sn-FeOOH NRs, respectively. The immersed FTO substrate was acquired by a modulated hydrothermal method. The FTO glass substrate (1 × 2 cm²) cleaned with ethanol and subsequently rinsed with deionized (DI) water was placed with the conducting side facing down in a Teflon-lined autoclave. FeOOH NRs were grown in 20 mL of an aqueous solution containing 0.15 M FeCl₃ and 40 μL of HCl at 100 °C for 6 h. After FeOOH NRs on FTO were thoroughly washed with DI water to remove the salty residue, it was annealed at 550 °C for 2 h to prepare Fe₂O₃ NRs on the FTO substrate.

**Synthesis of Sn-Doped Fe₂O₃ NRs Array.** Tin dichloride dehydrate (SnCl₂·2H₂O, 0.05 mol) was dissolved in 100 mL of ethanol. The solution was then transferred into a conical flask, sealed, and stirred at 70 °C for 4 h. To synthesize two types of Sn-doped Fe₂O₃ NR arrays, FTO glass substrates coated with FeOOH and Fe₂O₃ NR arrays were immersed in the Sn-precursor for 24 h at room temperature. The immersed FTO glass substrates were finally sintered at 550 °C for 2 h in a muffle furnace under atmosphere. Two types of Sn-doped Fe₂O₃ NR arrays were obtained, labeled as samples Sn-Fe₂O₃ and Sn-FeOOH NRs, respectively.

**Characterization.** The crystal structure of the samples was investigated by powder X-ray diffraction (XRD, Bruker D8 advance) using Cu Kα (λ = 1.5406 Å) radiation. The morphology information of Fe₂O₃, Sn-Fe₂O₃, and Sn-FeOOH NRs on the FTO substrate was acquired by a field emission scanning electron microscope (SEM, S-4800, Hitachi). High-resolution transmission electron microscopy (HRTEM) images and element mapping were acquired from a Tecnai G2 F30 microscope. UV–vis absorption spectra (200–1200 nm) were measured using a Varian Cary 50 UV–vis spectrophotometer. X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB-250Xi photoelectron spectroscope to obtain information on the valence state of the Fe, Sn, and O ions.

**PEC Measurements.** The electrochemical characteristics of as-synthesized samples were evaluated by photocurrent density curves, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and Mott–Schottky plots in the Zanner CIMPS electrochemical workstation (Germany) using a three-electrode cell in 1 M KOH (pH 13.6) solution. A Pt wire and a Ag/AgCl (Hg/HgO) in saturated KCl (KOH) were used as counter electrode and reference electrode, respectively, and a 300 W Xe lamp (CEL-HXF 300, Beijing Au-light, China) was employed as the incident light source to study the PEC response of the samples. The H₂ evolution experiments were carried out in a gas-closed circulation system under a 100 W Xe lamp. In a typical reaction, the catalyst film (1 × 1 cm²) was immersed in a 0.5M H₂SO₄ aqueous solution (80 mL of distilled water + 22.5 g of CuSO₄·5H₂O) in Pyrex cell with a side window.

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