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WO₃@Fe₂O₃ Core-Shell Heterojunction Photoanodes for Efficient Photoelectrochemical Water Splitting

Guobing Mao[1], Heng Wu[1,4], Tianyang Qiu[2], Dingjie Bao[1], Longjie Lai[1], Wenguang Tu[3]* and Qi Liu[1]*

[1]_School of Materials Science and Engineering, Anhui Polytechnic University, Wuhu, Anhui 241000, China_
[2]_Key Laboratory of Modern Acoustics (MOE), Institute of Acoustics, School of Physics, Eco-materials and Renewable Energy Research Center (ERERC), National Laboratory of Solid State Microstructures, Collaborative Innovation Center of Advanced Microstructures, Jiangsu Key Laboratory for Nano Technology, Nanjing University, Nanjing 210093, China_
[3]_School of Science and Engineering, The Chinese University of Hong Kong, Shenzhen, Guangdong 518172, China_
[4]_School of Mechanical Engineering, Anhui Institute of Information Technology, Wuhu, Anhui 241100, China_

ABSTRACT Photoelectrochemical (PEC) hydrogen production from water splitting is a green technology to convert solar energy into renewable hydrogen fuel. The construction of host/guest architecture in semiconductor photoanodes has been proven to be an effective strategy to improve solar-to-fuel conversion efficiency. In this study, WO₃@Fe₂O₃ core-shell nanoarray heterojunction photoanodes are synthesized from the _in-situ_ decomposition of WO₃@Prussian blue (WO₃@PB) and then used as host/guest photoanodes for photoelectrochemical water splitting, during which Fe₂O₃ serves as guest material to absorb visible solar light and WO₃ can act as host scaffolds to collect electrons at the contact. The prepared WO₃@Fe₂O₃ shows the enhanced photocurrent density of 1.26 mA cm⁻² (under visible light) at 1.23 V. vs RHE and a superior IPEC of 24.4% at 350 nm, which is higher than that of WO₃@PB and pure WO₃ (0.43 mA/cm⁻² and 16.3%, 0.18 mA/cm⁻² and 11.5%) respectively, owing to the efficient light-harvesting from Fe₂O₃ and the enhanced electron-hole pairs separation from the formation of type-II heterojunctions, and the direct and ordered charge transport channels from the one-dimensional (1D) WO₃ nanoarray nanostructures. Therefore, this work provides an alternative insight into the construction of sustainable and cost-effective photoanodes to enhance the efficiency of the solar-driven water splitting.
Keywords: host/guest photoelectrodes, WO₃, a-Fe₂O₃, core-shell nanostructures, one-dimensional nanoarray
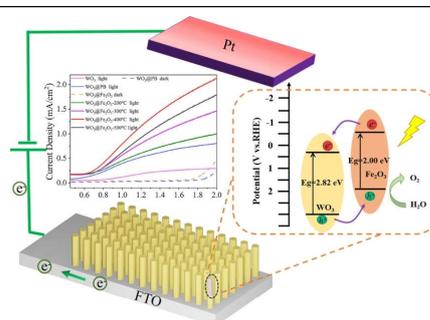
■ INTRODUCTION

Converting solar energy into renewable chemical fuels has been proven as one of the promising approaches to tackle the critical energy challenges and the environmental problems.[1,2] Photoelectrochemical (PEC) splitting water into hydrogen fuel conducted by semiconductor-based photoelectrodes can realize the storage of solar energy in the form of chemical energy.[3] Since Fujishima and Honda firstly conducted the pioneering PEC water splitting via TiO_2 films as the photoanodes, significant efforts have been made to explore appropriate semiconductor-based photoanodes to conduct efficient PEC water splitting from the factors such as the solar energy harvesting, the diffusion length of the charge carriers, and the photoanode stability. However, using single semiconductors such as TiO_2, WO_3, ZnO and a-Fe_2O_3 as photoanodes is difficult to meet the critical factors of PEC water splitting simultaneously.[4-7] For example, compared with the semiconductors with smaller band gap, the material with larger band gap possesses resistance photocorrosion, but the weakened light absorption capacity limits the improvement of PEC performace.[8-10]

Among the semiconductor materials for PEC water splitting, WO_3 is the widely researched n-type semiconductor due to its excellent optical properties, stability, and suitable band structure (of 2.5-2.8 eV).[11] WO_3 not only possesses high electron hole mobility (12 cm^2 V^{-1} s^{-1}) but also has deep carry diffusion length (~150 nm). However, the insufficient visible light adsorption restricts the im-

proved efficiency of PEC water splitting.[12-14] Inspired by the synergistic effects of a tree trunk for mass transport and leaves for light absorption in natural photosynthesis, host/guest multicomponent architectures have been explored for efficient PEC water splitting, during which a highly dispersed light absorber acting as the guest material is deposited onto nanostructured host scaffolds.[15-17] Recently, combining WO_3 with other semiconductors to construct host/guest heterojunction structure, such as g-C_3N_4/WO_3,[17,18] TiO_2/WO_3,[19-22] and WO_3/a-Fe_2O_3,[23-25] can effectively improve the visible light adsorption and the transfer of charge carriers, thus achieving considerable PEC performance. Furthermore, one-dimensional (1D) nanostructure arrays with a reduced quantity of defects and fewer grain boundaries could provide direct and ordered channels for charge transport.[26-29]

Here, we report a novel and facile method to prepare WO₃@Fe₂O₃ core-shell nanoarray heterojunction photoanodes via _in situ_ transformation from WO₃@Prussian blue (WO₃@PB), during which WO₃@PB on flourine-doped tin oxide (FTO) was prepared by the hydrothermal growth of WO₃ nanorod arrays and subsequent electrodeposition of PB layer on WO₃ nanorod arrays. The optimized WO₃@Fe₂O₃ prepared at 400 ℃ achieves the enhanced PEC performance with the photocurrent density of 1.26 mA cm⁻² at 1.23 V. vs RHE and a superior IPEC of 24.4% at 350 nm, which is higher than that of WO₃@PB and pure WO₃ (0.43 mA/cm⁻² and 16.3%, 0.18 mA/cm⁻² and 11.5%), respectively. It indicates that the formation of host/guest architecture in WO₃@ Fe₂O₃ core-shell

shell nanorod array heterojunction photoanodes.

The phases of as prepared samples are determined by the powder X-ray diffraction (XRD) patterns (Figure 1a). The diffraction peaks of WO_3 film are indexed to hexagonal-phase WO_3 (JCPDS 85-2460). Compared to pure WO_3 film, all characteristic peaks of WO_3@PB film are attributable to WO_3 (JCPDS 85-2460) and $Fe_4[Fe(CN)_6]_3$ (JCPDS 01-0239),[32-34] indicating the successful deposition of PB nanoparticles on the WO_3 nanorod arrays. For Fe_2O_3 thin film directly prepared from the annealing treatment of PB film, there are two characteristic peaks at 35° and 63°, which can be well assigned to the (201) and (220) planes of hexagonal Fe_2O_3 (JCPDS 40-1139). The characteristic peaks of hexagonal Fe_2O_3 also appear in the WO_3@Fe_2O_3 sample and no other redundant peaks appear, indicating that the PB completely transformed into Fe_2O_3 on the surface of WO_3 nanorod arrays. In order to explore the effect of heat temperature on the sample treatment, WO_3@PB samples were annealed at 200, 300, 400 and 500 ℃. The calcination temperature has a significant effect on the phase structure of the final products. No corresponding characteristic peaks of Fe_2O_3 were observed (Figure 1b), because the PB transformed into amorphous Fe_2O_3 after the heat treatment at 200 and 300 ℃.[35-37] Hu et al.[36] calcined PB with a particle size about 100-150 nm at 250 ℃, and amorphous Fe_2O_3 was obtained. As the calcination temperature increases, the phase of the final products changes from amorphous to crystal. When rising to 400 and 500 ℃, the corresponding characteristic peaks located at 35° and 63° were observed, indicating the crystalline Fe_2O_3 formed on the surface of WO_3 nanorod arrays.

As shown in Figure 2a, the scanning electron microscopy (SEM) image illustrates the uniform polygonal morphology of WO_3 nanorod arrays with the diameter of approximately 100 nm. The surface of WO_3 nanorod arrays becomes rough (Figure 2b) after the in situ deposition of PB, indicating the successful growth of PB nanoparticles on the WO_3 nanorod arrays. The morphology of WO_3 nanorod arrays is well preserved after the heat treatment for preparing WO_3@Fe_2O_3 nanorod arrays (Figure 2c, d). The surface of WO_3@Fe_2O_3 nanorod arrays becomes rougher with abundant pores, which greatly improves the specific surface area of WO_3@Fe_2O_3 nanorod arrays, resulting in more exposed catalytic

Scheme 1. Schematic illustration of the synthesis process of WO_3@Fe_2O_3.

nanoarray heterojunction photoanode induces the efficient light-harvesting from the Fe_2O_3 with the narrow bandgap as guest material, the enhanced electron-hole pairs separation from the formation of type-II heterojunctions, and the direct and ordered charge transport channels from the 1D host WO_3 nanoarray nanostructures. This work provides an alternative insight into the construction of sustainable and cost-effective photo-anodes to enhance the efficiency of the solar-driven water splitting.

■ RESULTS AND DISCUSSION

The synthesized processes of WO_3@Fe_2O_3 core-shell nanorod array heterojunction photoanodes are shown in Scheme 1. Firstly, WO_3 seed layer was got by spin-coating the tungstic acid solution on FTO glass and then annealing in the muffle furnace. Then, WO_3 nanorod arrays were vertically aligned on FTO surface by the hydrothermal method.[30] Subsequently, the PB layer was deposited on the surface of WO_3 nanorod arrays via the simple electrochemical deposition method[31] to form WO_3@PB nanorod arrays. Finally, PB on WO_3 surface would in situ transform into Fe_2O_3 by the annealing treatment to obtain WO_3@Fe_2O_3 core-

Figure 1. XRD and partial enlarged XRD patterns of (a) FTO, WO_3, WO_3@PB, Fe_2O_3, and WO_3@Fe_2O_3. (b) WO_3@Fe_2O_3 prepared at different heat treatment temperatures.

Figure 2. SEM images of (a) WO_3, (b) WO_3@PB, and (c, d) WO_3@Fe_2O_3 prepared at 400 ℃.
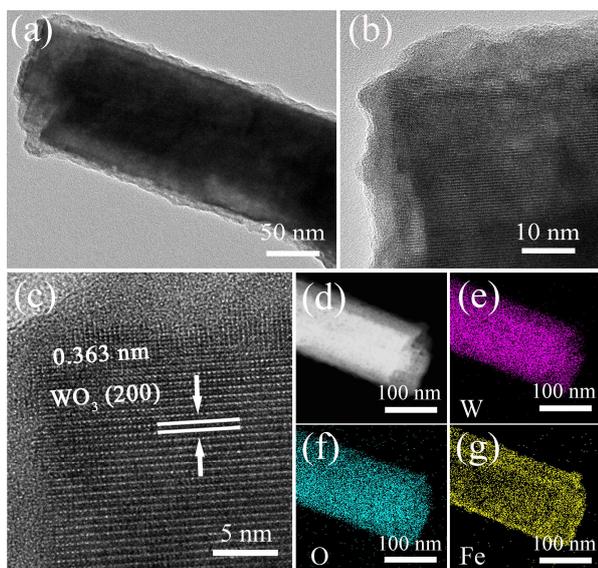
Figure 3. TEM images of (a,b) $WO_3@Fe_2O_3$, (c) HRTEM image of $WO_3@Fe_2O_3$, (d-g) Elemental mapping images of $WO_3@Fe_2O_3$.

sites. Moreover, the porous structure could lead to the reflection and absorption of light, probably improving the photon absorption efficiency.

The high-resolution TEM (HRTEM) image (Figure 3a) showed one single WO_3 nanorod with a diameter of about 120 nm. Moreover, the ultra-small Fe_2O_3 nanoparticles are uniformly distributed on the surface of WO_3 nanorod to form a porous shell with a thickness of about 10 nm (Figure 3a, b). As shown in Figure 3c, the lattice fringe with an interplanar spacing of 0.365 nm is corresponding to (200) crystallographic plane of hexagonal WO_3. TEM-energy-dispersive X-ray spectrometry (EDS) elemental mappings (Figure 3d-g) furtherly confirmed the uniform distribution of Fe_2O_3 nanoparticles on the surface of WO_3 nanorod.

X-ray photoelectron spectroscopy (XPS) analysis was employed to further investigate the valence state of all atoms (Figure 4). The survey spectrum suggests the presence of W, O and Fe elements
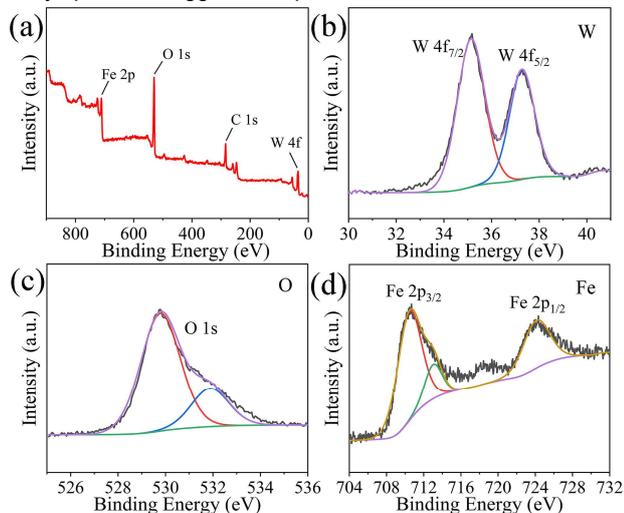
in $WO_3@Fe_2O_3$ heterojunction (Figure 4a). The high-resolution XPS spectra of W 4f (Figure 4b) show two characteristic peaks of W $4f_{7/2}$ at 35.8 and W $4f_{5/2}$ at 37.4 eV, indicating the oxidation state of W^{6+}.[38] The O 1s spectrum of the sample can be subdivided into one peak at 531.9 eV attributed to the adsorption of water and oxygen from hydroxide on the surface[39,40] and the other strong peak at 529.8 eV belonging to the lattice oxygen of metal oxide (Figure 4c). The Fe 2p spectra at higher resolution (Figure 4d) exhibit two binding energy peaks at 724.4 eV (Fe $2p_{1/2}$) and 710.8 eV (Fe $2p_{3/2}$) with a characteristic satellite peak at 719.1 eV, which is the typical characteristic of Fe^{3+}. Therefore, the successful fabrication of the $WO_3@Fe_2O_3$ composite can be confirmed.

The PEC performances of the fabricated electrodes were measured in a three-electrode electrochemical cell with 0.1 M Na_2SO_4 as electrolyte under irradiation using a 300 W Xe arc lamp with a UV cutoff filter ($\lambda > 420$ nm) (Figure 5). The photoelectric response of the prepared electrodes was evaluated by linear sweep voltammograms (LSV) (Figure 5a). The photocurrent of $WO_3@Fe_2O_3$ increases with the increase of treatment temperature from 200 to 400 ℃ and then decreases from 400 to 500 ℃. The photocurrent density of $WO_3@Fe_2O_3$-400 photoanode is continuously strong in the linearly swept from 0.6 to 2.0 V (RHE) in comparison with the others, indicating that 400 ℃ is the optimal temperature for sample treatment. The transient photo-current curves of as-synthesized photoanodes at 1.23 V (vs. RHE) under light irradiation were presented in Figure 5b. For all the photoanodes, the photocurrents appeared under light irradiation and then disappeared once the light was turned off, implying rapid photoresponsive properties of the obtained photoanodes. The photocurrent density of $WO_3@Fe_2O_3$ treated at 200, 300, 400 and 500 ℃ are 0.68, 0.80, 1.26 and 0.98 mA/cm^2, respectively. The highest photocurrent density up to 1.26 mA/cm^2 was obtained over $WO_3@Fe_2O_3$-400 photoanode, which is about 3.0 times that of $WO_3@PB$ (0.43 mA/cm^2) and 7.0 times that of pure WO_3 (0.18 mA/cm^2). Bare Fe_2O_3 shows weak photocurrent density due to fast recombination of photogenerated carriers (Figure S1). When light reaches on the Fe_2O_3 photoanode, the increase in photocurrent is accompanied by a nearly instant rapid decay. Ultrafast charge recombina-

Figure 4. XPS analysis of $WO_3@Fe_2O_3$: (a) survey spectra, (b) W 4f, (c) O 1s, (d) Fe 2p.
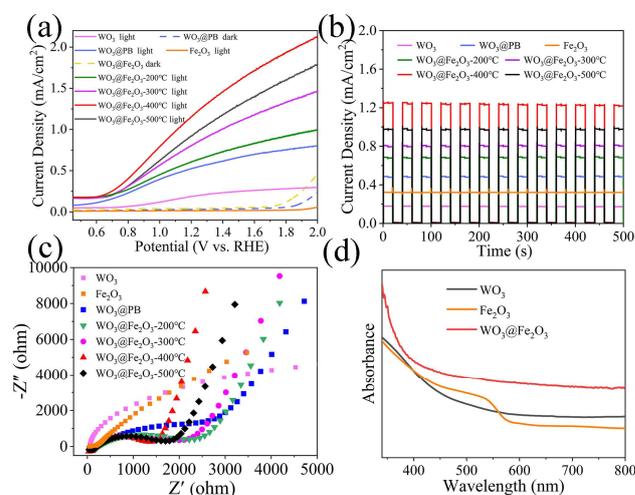
Figure 5. (a) LSV (scan rate: 5 mV s⁻¹), (b) photocurrent (I-t), (c) EIS results, (d) UV-vis absorption spectra for prepared samples.

2208027

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Chin. J. Struct. Chem. **2022**, 41, 2208025-2208030

DOI: 10.14102/j.cnki.0254-5861.2022-0086

tion in Fe_2O_3 can be effectively overcome by compounding with other semiconductors or doping different elements.[41-43]

The electrochemical impedance spectroscopy (EIS) measurements were employed to further investigate the charge transport kinetics of these photoanodes, as shown in Figure 5c and Figure S2. The smaller semicircle radius represents the smaller charge transfer impedance and the higher separation efficiency of the photogenerated electrons-hole pairs.[44] The semi-circle diameters of all prepared $WO_3@Fe_2O_3$ are much smaller than that of WO_3 @PB and WO_3, indicating better interface charge transfer between WO_3 and Fe_2O_3. $WO_3@Fe_2O_3$-400 shows the smallest semi-circle compared with other heat treatment temperatures, which indicates that this sample has the fastest interfacial charge transfer rate and the best separation of photogenerated electrons-hole pairs in $WO_3@Fe_2O_3$-400. The fitted EIS results of photoanodes are summarized in Table S1, which basically reveals the analogous variation trends in LSV and I-t results.

For photoelectrocatalysis, efficient photon utilization and matched band structure for catalytic materials are of vital importance. Thus, we utilized UV-visible (UV-vis) diffuse reflectance spectra to monitor the light adsorption capacity of pristine WO_3 and $WO_3@Fe_2O_3$ (Figure 5d). The bandgap valences of all samples are estimated by UV-vis adsorption spectra through a related curve of $(\alpha h\nu)^{1/2}$ versus the mode of photon energy, and the bandgaps of WO_3 and Fe_2O_3 were calculated to be 2.82 and 2.00 eV, respectively. After Fe_2O_3 was grown on the surface of WO_3 nanorods to form a heterostructure, the mode of interband tansition of electrons changed, resulting in the reduction of the band gap width and the enhancement of light adsorption capacity. Furthermore, the porous structure of Fe_2O_3 provides a higher photon receiving area and reduces the non-ultilization of optical wave caused by reflection on the material surface. To be specific, when the light shines on the surface of the nanorods, photon will enter the hole and be reflected many times in the hole until absorbed.

The incident photon-to-current conversion efficiency (IPCE) measurement was conducted to investigate the influence of light absorption. The IPCE of $WO_3@Fe_2O_3$ increases with increasing

the treatment temperature from 200 to 400 ℃ and then decreasing it from 400 to 500 ℃ (Figure 6a), showing a similar trend with the photocurrent of $WO_3@Fe_2O_3$. $WO_3@Fe_2O_3$-400 shows the highest IPCE value, which is up to 24.4% at 350 nm. The IPCE results reveal that the deposition of Fe_2O_3 on the surface of WO_3 enhances the light absorption capacity. Therefore, the IPCE value of $WO_3@Fe_2O_3$ is significantly improved compared with that of $WO_3@PB$. These results show that host/guest approach can effectively enhance the photoelectrochemical performance of WO_3 film. Gratzel et al constructed $WO_3@Fe_2O_3$ host/guest photoanodes which show a ca. 20% increase in photocurrent as compared to Fe_2O_3.[45] $WO_3/Ti-Fe_2O_3$ photoanode was designed with improved PEC water splitting performance owing to charge transfer enhancement of WO_3/Fe_2O_3 interface.[46] This host/guest WO_3 @Fe_2O_3 derived from PB not only facilitates the charge separation but also boosts the light absorption.

In order to prove the charge transfer between WO_3 and Fe_2O_3, the photoluminescence (PL) spectra of $WO_3@Fe_2O_3$ have been investigated (Figure 6b). The PL intensity of $WO_3@Fe_2O_3$ is much lower than that of Fe_2O_3 and WO_3 films, confirming the efficient separation of the photogenerated electrons-hole pairs. Mott-Schottky plots of pristine WO_3 and Fe_2O_3 films were employed to investigate the band alignment information (Figure 6c). Both Mott-Schottky plots of pristine WO_3 and Fe_2O_3 exhibit positive slopes, indicating the n-type semiconductor feature of WO_3 and Fe_2O_3. The results display that the flat band potentials of WO_3 and Fe_2O_3 are 0.51 and -0.11 V, respectively. Combined with the aforementioned results of optical bandgap estimation, the conduction band (CB) and valence band (VB) positions of WO_3 are calculated to be 0.42 and 3.24 eV, and the CB and VB positions of Fe_2O_3 are located at -0.21 and 1.79 eV. Therefore, a possible schematic illustration for energy-level alignment of $WO_3@Fe_2O_3$ is suggested in Figure 6d. It can be seen that WO_3 and Fe_2O_3 show a well staggered band alignment with the type II heterojunction. Due to the higher CB of Fe_2O_3 than WO_3, the photogenerated electrons of Fe_2O_3 can be immediately delivered to the CB of WO_3 via the direct and ordered charge transport channels from the one-dimensional (1D) WO_3 nanoarray nanostructures, while photogenerated holes of WO_3 can transfer to the VB of Fe_2O_3, which hinders the fast recombination of electron-hole pairs and thus improves PEC activity.

■ CONCLUSION

In summary, $WO_3@Fe_2O_3$ core-shell nanoarray heterojunction photoanodes were prepared by *in-situ* decomposition of WO_3 @PB precursor at different temperature. The optimized $WO_3@$ Fe_2O_3 prepared at 400 ℃ showed efficient PEC performance with the photocurrent density of 1.26 mA/cm² at 1.23 V vs. RHE, which is about 3.0 times that of $WO_3@PB$ (0.43 mA/cm²) and 7.0 times that of pure WO_3. The efficient PEC performance of $WO_3@Fe_2O_3$ is attributed to the construction of type-II core-shell heterojunctions, which enhances the visible light absorption and facilitates the separation of photo-generated electron-hole pairs. This work provides an alternative insight into the construction of sustainable and cost-effective photoanodes to enhance the efficiency of the solar-driven water splitting.

Figure 6. (a) IPCE plots, (b) PL of prepared samples, (c) Mott-Schottky curves of WO_3 and Fe_2O_3, (d) Schematic of the charge transfer and separation in the $WO_3@Fe_2O_3$ and the PEC working mechanism for water splitting.

■ EXPERIMENTAL

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Materials. All reagents were obtained from commercial sources and used as received without further purification.

Synthesis of WO₃ and WO₃@Fe₂O₃ Films. The WO$_3$ nanorod arrays were synthesized with the hydrothermal method modified from previously reported method.[30] The electrochemical deposition of PB layer on WO$_3$ nanorod arrays was conducted in the three-electrode system at room temperature, during which the FTO with WO$_3$ film, the platinum plate, and the Ag/AgCl were used as the working electrode, counter electrode, and reference electrode, respectively. The electrolytes were composed of 1 mM $K_3Fe(CN)_6$, 1 mM $FeCl_3\cdot6H_2O$, and 5.0 mM KCl. The PB layers were deposited on the surface of WO$_3$ by applying a constant potential at 0.3 V for 100 s. The obtained samples were washed with deionized water and then dried at 100 ℃ for 1 h. Then, WO$_3$@PB nanorod arrays were heated at the different temperature of 200, 300, 400, and 500 ℃, which were defined as WO$_3$@Fe$_2$O$_3$-200, WO$_3$@Fe$_2$O$_3$-300, WO$_3$@Fe$_2$O$_3$-400 and WO$_3$@Fe$_2$O$_3$-500, respectively. The heating and cooling rates were 4 and 5 ℃ min^{-1}. As a comparison, Fe$_2$O$_3$ thin film was prepared by annealing the PB film directly.

Characterization. The phase structures of the prepared samples were studied with an X-ray diffractometer with Cu Kα radiation of λ = 1.5406 Å. The Field-emission scanning electron microscopy (FESEM) was tested by S-4800 (Japan) instrument. The TEM data, elemental mapping, and energy dispersive X-ray spectroscopy (EDS) values were measured using JEOL JEM-2100 F (USA). The X-ray photoelectron spectroscopy (XPS) measurements were obtained using Thermo Fisher Scientific K-Alpha (USA), and the binding energy was calibrated with C 1s at 284.8 eV. The UV visible light adsorption spectra were using a Shimadzu UV-3600 with an 0.1 nm interval in the range of 185-800 nm, and the spectra were transformed from reflection into absorbance by the Kubelka-Munk Method. The photoluminescence spectra analysis was performed using a Horiba Fluorolog 3-22 fluorometer with an excitation wavelength of 520 nm and an emission spectrum scanning range of 550-850 nm.

Electrochemical Measurements. The electrochemical measurements were recorded at room temperature (25 ℃) in cell quartz with a three-electrode system configurations, during which thin-film FTO, Ag/AgCl, Pt mesh, and 0.1 M Na$_2$SO$_4$ solution were used as the working electrode, reference electrode, counter electrode, and electrolyte, respectively. The 300 W Xe lamp was used as light source by using a UV cutoff filter (λ > 420 nm) to get visible light. The Nyquist plots were measured in the frequency range between 0.01 and 10^5 Hz at 1.23 V vs. RHE under dark conditions with an AC voltage perturbation of 10 mV. The Mott-Schottky measurements were conducted in dark conditions at 2000 Hz.

◼ AUTHOR INFORMATION

Corresponding authors. Emails: modieer_67@ahpu.edu.cn and tuwenguang@cuhk.edu.cn

◼ COMPETING INTERESTS

The authors declare no competing interests.

◼ ADDITIONAL INFORMATION

Supplementary information is available for this paper at http://manu30.magtech.com.cn/jghx/EN/10.14102/j.cnki.0254-5861.2022-0086

For submission: https://mc03.manuscriptcentral.com/cjsc

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