Electrochemical synthesis of p-Type Zn-Doped α -Fe₂O₃ nanotube arrays for photoelectrochemical water splitting

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Experimental

Preparation of ZnO nanorod arrays

ZnO nanorod arrays were electrodeposited on transparent conductive substrate (ITOor FTO- coated glass) through a method previously reported by our group. Before the electrodeposition, the transparent conductive glass substrate were ultrasonically cleaned successively in acetone, ethanol and deionized water. The ZnO nanorod arrays were electrodeposited on the ITO/FTO substrate in a three-electrode cell, where the ITO/FTO substrates were used as the working electrode, a Pt foil and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. An aqueous solution containing 0.2 mM $Zn(AC)_2$ and 0.1 M KCl with temperature of 85 °C was used as the electrolyte, which was continuously bubbled with pure O₂ gas. An electrochemical analytical instrument (CHI 660c) was used to apply a potential of -1 V vs SCE on the ITO/FTO substrates for 2 hours to electrodeposit the ZnO nanorods arrays on the ITO/FTO substrates. After the electrodeposition, the substrates with the ZnO nanorods arrays were taken out of the cell, and were washed with deionized water and dried by blowing N₂.

Preparation of Zn-doped p-type α-Fe₂O₃ nanotube arrays

The α -Fe₂O₃ nanotube arrays were prepared by anodic electrodeposition in a three-electrode cell, where the ITO/FTO substrates with the ZnO nanorods arrays were used as the working electrode, a Pt foil and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. An aqueous solution containing 5 mM FeCl₂ (pH=4) with an temperature of 75 °C was used as the electrolyte. An anodic potential of 1 V vs SCE were applied on the ITO/FTO substrates with the nanorod arrays for a certain time to enable the oxidation of the Fe²⁺ ions in the electrolyte to Fe³⁺ irons, which was followed by the precipitation of Fe³⁺ irons into amorphous γ -FeOOH on the ZnO nanorods. During this process, the ZnO nanorods were gradually dissolved by the acidic solution and anodic potential. After 2.5 min electrodeposition, the

ZnO nanorods were completely dissolved, which is confirmed by the absence of the peak signals for the ZnO in the X-ray diffraction spectrum (see Figure S1). Some of the Zn²⁺ ions dissolved in the electrolyte around the working electrode were in situ incorporated into the γ -FeOOH intermediates and would serve as p-type dopants for the α -Fe₂O₃. After the electrodeposition, the substrates with the γ -FeOOH nanotubes were taken out of the cell, washed with deionized water and dried by blowing N₂, and finally annealed in a muffle furnace at 520°C for 2 hours in atmosphere after a rising rate of 2°C/s, so as to convert the γ -FeOOH intermediates to α -Fe₂O₃ nanotubes. The chemical reactions are as follows:

 $ZnO + 2H^+ \Rightarrow Zn^{2+} + H_2O$

 $Fe^{2+} \Rightarrow Fe^{3+}$ (1 V vs SCE)

 Fe^{3+} + 2H₂O → FeOOH + 3H⁺ (Zn incorporated into the FeOOH during this process) 2FeOOH → Fe₂O₃+ H₂O (annealing at 520°C)

Preparation of Zn-free α-Fe₂O₃ films

The Zn-free α -Fe₂O₃ films were prepared using bare FTO glass substrates as the working electrodes and though the same anodic electrodeposition method used to fabricate the Zn-doped α -Fe₂O₃ nanotubes.

Photoelectrochemical and electrochemical impedance characterization

To investigate the photoelectrochemical properties of the as-prepared samples, a three-electrode cell was used. The Zn-doped α -Fe₂O₃ nanotube arrays were used as working electrode and a Pt foil and a SCE were used as counter electrode and reference electrode, respectively. An aqueous solution of 1 M NaOH was used as the electrolyte. A light with constant intensity of 100 mW cm⁻² from a 500W Xe lamp passed through an AM 1.5G filter was employed as the light source. An electrochemical analytical instrument (CHI 600C) was used to perform the linear Sweep voltammetry (with a

potential sweep rate of 5mV s⁻¹) and the Mott-Schottky measurements (in dark and with

AC frequencies of 2500 HZ). The measured potentials against SCE were converted to 1

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.059 \text{pH} + E^{0}_{\text{SCE}}$$

Wherein E_{RHE} is the converted potentials vs RHE, E_{SCE}^0 is the potential of SCE and is 0.242V at 25°C, E_{SCE} is the experimentally measured potential against SCE.

Supporting figures and results



Fig. S1 XRD spectrum collected from the amorphous γ -FeOOH sample prepared with an electrodeposition time of 2.5 min, from which no peaks for ZnO (JCPDS card No. 36-1451, the diffraction peaks highlighted with red line) can be observed, suggesting that the ZnO was fully dissolved.



Fig. S2 SEM images of the ZnO nanorod arrays prepared by electrochemical deposition.



Fig. S3 Full XPS spectrum collected from the Zn-doped α -Fe₂O₃ nanotubes prepared with an electrodeposition time of 10 min.



Fig. S4 XPS binding energy of Fe 2p in Zn-doped α -Fe₂O₃ nanotubes prepared with an electrodeposition time of 10 min.



Fig. S5 (a) (b) High resolution SEM images of some broken α -Fe₂O₃ nanotubes exhibiting closed tops and hollow structures; (c) (d) SEM images of some α -Fe₂O₃ nanotubes unintentionally damaged during the sample preparation process for SEM observation.



Fig. S6 SEM image of the α -Fe₂O₃ film without Zn doping. The α -Fe₂O₃ film was directly electrodeposited on FTO glass substrate with the same experimental conditions as those used to fabricate the Zn-doped α -Fe₂O₃ nanotubes.



Fig. S7 (a) Linear sweep voltammograms of the α -Fe₂O₃ film without Zn doping, in 1M NaOH solution at a scan rate of 5mV s⁻¹ and potentials from 0.3 to -0.5 V vs SCE, under simulated AM 1.5G illumination of 100 mW cm⁻². (b) Mott-Schottky plot of the Zn-free α -Fe₂O₃ film.

The Zn-free α -Fe₂O₃ film exhibits n-type photoresponse with a photocurrent less cathodic than the dark current. The charge carrier density was calculated to be N_d=3.14×10¹⁸ cm⁻³ through the slope of the linear region in the Mott-Schottky plot.



Fig. S8 UV-Vis absorption spectra of the α -Fe₂O₃ film prepared with electrodeposition time of 10 min, and Zn-doped α -Fe₂O₃ nanotubes prepared with electrodeposition time of 5 min, 10 min and 15 min. The α -Fe₂O₃ film shows much weaker light absorption ability than the nanotubes.



Fig. S9 XPS binding energies of Zn 2p in Zn-doped α -Fe₂O₃ nanotubes prepared with an electrodeposition time of 5 min, 10 min and 15min.

The atomic percentages of Zn in the surface of the α -Fe₂O₃ nanotubes are 7.8 at. % (5min), 6.2 at.% (10min) and 2.9 at.% (15min) relative to Fe.



Fig. S10 Mott-Schottky plots and the calculated acceptor densities of the Zn-doped α -Fe₂O₃ nanotubes prepared with electrodeposition time of 5 min, 10 min and 15 min.

It can be seen that the acceptor densities decreases as the electrodeposition time prolongs. The decreased acceptor densities could be due to the decreased Zn doping degree, as was calculated from the XPS analyses (Fig. S9).