Construction of Fe(OH)$_3$-ZnO/NF nanotube arrays with enhanced performance for water splitting

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Abstract: Well-aligned hierarchical hollow nanoarrays containing ZnO core and Fe(OH)$_3$ nanotube shell have been synthesized via simple one-step hydrothermal method and etching at room temperature. The obtained catalyst has a high specific surface area, a large number of catalytic active sites and good chemical stability. The resulting Fe(OH)$_3$-ZnO/NF nanotubes exhibit promising behavior in alkaline solution. When the current density is 10 mA cm$^{-2}$, the HER and OER overpotentials ($\eta_{10}$) of Fe(OH)$_3$-ZnO/NF are 190 and 388 mV, respectively.

1. Introduction

Energy and environment are two prominent issues that restrict the development of human society. In current, the traditional fossil fuels dominate the main energy use structure, despite it also brings abundant environmental pollution[1]. Numerous efforts are being strived for appropriate alternative power sources. As a renewable clean energy, hydrogen is considered to be the best alternative to traditional fossil energy[2]. Electrocatalytic water splitting reaction provides an uncomplicated and feasible method for preparing hydrogen, has attracted lots of attentions[3-4]. Due to the sluggish kinetics and slow rates of gas release at a low overpotential of both OER and HER, which are expected to be improved further. The electrocatalysts that can reduce overpotentials and accelerate the reaction rate at the same time are regarded as an ideal method[5-6]. Hence, it is extremely urgent to develop the efficiency, low-cost and sustainability of electrocatalysts.

Considerable research has been used to develop materials based on transition metal compounds, including phosphides[7], sulfides[8] and hydroxide[9]. As reported, the hydroxide of iron can promote the oxidation of water through the change of valence state of Fe$^{3+}$[10]. The hollow structure has a better specific surface area and also exposing more active sites[11].

Herein, we have prepared the ZnO/NF hollow nanotubes via one-step hydrothermal method. Then, the Fe(OH)$_3$-ZnO/NF was obtained by etching ZnO through in-situ reaction (ZnO+Mn$^+$+H$_2$O $\rightarrow$ Zn$^{2+}$+M(OH)$_n$, M=Fe or Ni)[10]. As expected, the prepared Fe(OH)$_3$-ZnO/NF with above features exhibit lower overpotential (190 mV for HER and 388 mV for OER at 10 mA cm$^{-2}$), excellent activity and durability for water splitting in alkaline electrolyte.

2. Experiment

2.1 Synthesis of ZnO/NF

At the beginning of material preparation, a piece of commercial NF (1×3 cm) was sonicated in HCl solution (1 M) and ethanol solution for 30 minutes to remove surface stains. The nickel foam was
soaked in potassium permanganate solution for 20 minutes to activate the surface of the nickel foam. Next, disperse 20 mg Zn(N0₃)₂·6H₂O in a mixture of 50 ul Nafion, 100 ul isopropanol and 850 uL distilled water. The nickel foam was placed in the above solution and soaked for 10 min, waiting for it to dry and then calcining at 400 °C for 2 hours in a nitrogen atmosphere. Finally, the nickel foam loaded with the ZnO seed layer was grown in an autoclave at 95°C in a mixed solution of ammonia water and Zn(N0₃)₂·6H₂O. After taking ZnO/NF out of the reaction kettle, rinse with ethanol and deionized water respectively, and put it in an oven to dry for using.

2.2 Synthesis of nanorod Fe(OH)₃-ZnO/NF
The ZnO/NF was soaked in a 0.005 mol/L FeCl₃ solution for 10 min, then taking the sample out, rinsing and drying it with distilled water for later using.

2.3 Characterization
The phase composition of the prepared sample was tested by X-ray diffraction (XRD, Bruker D8 Discover). The morphology and microstructure of the sample were observed with a scanning electron microscope (FESEM Hitachi S-4800) and transmission electron microscope (TEM JEM-2100).

2.4 Electrochemical measurements
The complete hydrolysis performance of the material is tested using an electrochemical workstation (CHI660E), and all electrochemical tests are performed in 1 mol/L KOH aqueous solution. The three electrodes used in the test are: Fe(OH)₃-ZnO/NF working electrode with a size of 1 cm × 1 cm; platinum plate counter electrode; Ag/AgCl reference electrode. Use the following formula for potential calibration: ERHE = EAg/AgCl + 0.194 + 0.059 × pH.

3. Results and discussions

Fig.1. The XRD spectra of as-prepared samples
X-ray diffraction patterns of the Fe(OH)₃-ZnO/NF nanotube are shown in Fig. 1. The obvious diffraction peaks at 44.5°, 51.85° and 76.37° peak correspond to the (111), (200) and (220) crystal planes of Ni. What’s more, the new peaks at 31.77 °, 34.42 °, 36.25 °, 47.54 °, 56.60 °, 62.86° and 67.96 ° can be observed in as-prepared ZnO-NF are ascribed to the (100), (002), (101), (102), (110), (103) and (112) planes of ZnO. In Fe(OH)₃-ZnO/NF, the characteristic peaks of ZnO can still be observed but there is no obvious peak of Fe(OH)₃, which can be ascribed to that the ZnO cannot be completely etched away and the crystallinity of Fe(OH)₃ is weak.
Fig. 2. SEM of (a-c) ZnO/NF with magnification of 1K, 5K and 10K (d-f) Fe(OH)$_3$-ZnO/NF with magnification of 1K, 5K and 10K.

Fig. 3. (a) TEM of ZnO nanorod (b) HR-TEM of ZnO nanorod (c) TEM of Fe(OH)$_3$ nanotube (d) HR-TEM of Fe(OH)$_3$ nanotube

The morphology of samples is showed in Fig. 2. As revealed in Fig. 2a, a large amount of ZnO nanorods are uniformly loaded on the foamed nickel. The diameter of the dense nanorods is about ~100 nm, and there is no adhesion between them. Fig. 3(b) shows that the interplanar spacing of the nanorods is 0.289 nm, which is consistent with the ZnO(100) plane. After immersing ZnO-NF in FeCl$_3$ aqueous solution for etching reaction, according to the reaction: $3\text{ZnO} + 2\text{FeCl}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 + 3\text{ZnCl}_2$, we can get the nanotube array as shown in Figure 2d. As shown in Fig. 2f, it’s clearly that the composite sample presents a hollow tubular structure. In addition, this tubular structure can provide more channels for electron migration during hydrogen evolution and oxygen evolution. The TEM image in Fig. 3c shows that the nanotube wall is composed of many nanoparticles with a size of ~5 nm.
We further analyzed the active sites of composite materials and their contribution to electrocatalysis. Therefore, the electric double layer capacitance (Cdl), which is proportional to the electrochemical surface area (ECSA), is used for reasonable estimation and comparison. According to the cyclic voltammograms obtained at different scan rates (Figures 4a, b and c), the fitted Cdl of Fe(OH)$_3$-ZnO/NF is 8.89 mF cm$^{-2}$ (Figure 4d), which is much higher than NF (2.43 mF cm$^{-2}$). The high Cdl value means that the catalyst obtains more active sites for complete hydrolysis.

The performance of the HER and OER was evaluated via the linear sweep voltammetry (LSV). In order to comparison, bare NF and ZnO/NF were also tested. Fig. 5a and 5c display their polarization curves with iR correction. As shown in the Fig. 5a, Fe(OH)$_3$-ZnO/NF has good hydrogen evolution performance, and as the overpotential increases, the prepared hollow nanotube catalyst performs better. When the current density reaches -10 mA cm$^{-2}$, the required overpotential is as low as 190 mV, which is better than NF ($\eta_{10} = 264$ mV) and ZnO/NF ($\eta_{10} = 350$ mV). Compared with bare NF, the activity of ZnO/NF is slightly decreased, which indicates that the OER activity of ZnO is lower, which is
consistent with the properties of ZnO semiconductor materials. The $\eta_{10}$ of Fe(OH)$_3$-ZnO/NF is 388 mV, which is better than NF ($\eta_{10} = 431$ mV) and ZnO/NF ($\eta_{10} = 450$ mV).

4. Conclusion
In this work, the Fe(OH)$_3$-ZnO nanotube core-shell catalyst for water splitting was prepared by one-step hydrothermal and etching methods. Herein, the ZnO nanotubes directly grown on nickel foam can strengthen the contact between the active material and the conductive substrate and enhance the long-term stability of the electrocatalytic process. Subsequently, the Fe(OH)$_3$ nanoparticles accumulate on the surface of the nanorods. Due to the incomplete etching of ZnO, the catalyst can gradually form a core-shell nanotube structure. By evaluation, the composite catalyst exhibits a good performance in HER and OER.

Acknowledgments
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