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Full Length Article

Facile synthesis of pyrite-type binary nickel iron diselenides as efficient electrocatalyst for oxygen evolution reaction

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ABSTRACT

Pyrite-type binary nickel iron diselenides ($Ni_{0.5}Fe_{0.5}Se_2$) supported on carbon fiber cloth (CFC) as electrocatalysts for oxygen evolution reaction (OER) have been prepared by a facile two-step process. Firstly, binary $Ni_{0.5}Fe_{0.5}$ hydroxide nanosheets have been electrodeposited on CFC. Secondly, a solvothermal selenization process has been used to convert $Ni_{0.5}Fe_{0.5}$/CFC into $Ni_{0.5}Fe_{0.5}Se_2$/CFC. XRD shows that $Ni_{0.5}Fe_{0.5}Se_2$ on CFC has the typically octahedral crystalline. XPS proves the existence and valence of Ni, Fe and Se. SEM images show that $Ni_{0.5}Fe_{0.5}Se_2$ has novel pyrite-type octahedral morphology with uniform size and good dispersion on the surface of CFC. SEM elemental mapping images confirm the good distribution of Ni, Fe, Se element on CFC. TEM and SAED provide the clear diffraction rings of octahedral $Ni_{0.5}Fe_{0.5}Se_2$, which is consistent with the results of XRD. Furtherly, the effect of different ratio of Ni/Fe ($Ni_xFe_{1-x}Se_2$ x = 0, 0.2, 0.5, 0.8, 1) on OER performances has been systematically investigated. The electrochemical measurements results show that $Ni_{0.5}Fe_{0.5}Se_2$/CFC (x = 0.5) possesses the better electrocatalytic activity with the lower overpotential, Tafel slope and long-term stability than other samples. The enhanced activity of $Ni_{0.5}Fe_{0.5}Se_2$/CFC may be attributed to the intrinsic activity of binary $Ni_{0.5}Fe_{0.5}Se_2$ and faster electron transfer rate derived from CFC support.

1. Introduction

The severe energy crisis and demand for global environmental protection promote the intense pursue for renewable energy resources such as solar energy, wind energy, water power, etc [1–3]. Electrochemical water splitting has been regarded as an effective strategy for utilizing electricity produced by renewable energy resources. There are two half reactions including hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in water splitting, which needs electrocatalysts for improving efficiency of HER and OER [4–9]. Especially, multiple proton-coupled electron transfer and the formation of a relatively weak O—O bond during OER severely limited the enhancement of water splitting both in basic and acidic media [10,11]. Thus it is of vital importance to develop highly efficient OER electrocatalysts to accelerate water splitting. So far, noble metal oxides such as IrO_2 and RuO_2 have been the most excellent electrocatalyts for OER. However, the scarcity nature and high cost have prevented their application for industrialization [12,13].

Tremendous efforts have been made to explore non-precious OER electrocatalysts with earth-abundance and good activity [14,15]. Most of non-precious OER catalysts have been reported are metal oxides and (oxy) hydroxides [16,17] such as cobalt oxide (Co_3O_4) [18] and nickel hydroxide [19], demonstrating their promising electrocatalytic activity for OER. Moreover, researches reported that the activity of nickel oxides or hydroxides can be further enhanced by metal doping such as Fe [20,21] and etc. The doping of Fe with low cost and nontoxic elements can cause the change of electronic structure of Ni-based active sites and promote the formation of more real active sites for OER thus improving the catalytic activity [22]. Furthermore, metal doping has also been a strategy to solve the conductivity and provide the synergistic effect between metal and metal [23]. Likewise, metal selenides, as an important member of transition-metal chalcogenides (TMCs) have been speculated to be excellent electrocatalysts for OER such as NiSe [24], $NiSe_2$ [25,26] and Ni_3Se_2 [27]. Recently, Hu et al. synthesized Fe-doped $NiSe_2$ nanoplates for OER performing excellent electrocatalytic activity [28]. This research indicates that binary metal selenides may be more promising OER electrocatalysts uti-

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lizing synergistic effect among binary metals than single metal selenides. However, the systematic researches about binary metal selenides have been seldom reported and it is still an urgent task to control morphology and optimize the doped ratio of binary metal in promoting water splitting using an effective method [29].

Designing unique nanostructure with more active sites and enhanced intrinsic activity may be another choice to prepare high efficient metal selenides for OER. For example, Xie's group successfully synthesized hexagonal NiSe nanowire for electrochemical water oxidation [30]. Our group designed NiSe@NiOOH core-shell hyacinth-like nanostructures on nickel foam as robust electrocatalysts for OER [31]. Sun's group has prepared uniform NiSe nanowire film anchored on nickel foam (NF) with excellent catalytic activity and stability for OER [32]. On the other hand, the 3D free-metal OER electrode can obviously promote the leaching of oxygen bubbles, increase conductivity without further binder and facilitate electrolyte penetration [33–35]. Mai's group designed porous bimetallic selenide nanosheets using 3D CFC as substrate with good dispersion on the surface [36]. As a new kind of attractive electrode material, CFC with 3D structure has been proved to provide abundant paths to transfer electrons, which is favorable for promoting electrolyte diffusing in the electrode material [37]. Previous studies have confirmed that the enhanced nanostructures of active sites dispersed homogeneously by using 3D CFC [38]. Therefore it is an attractive strategy to anchor 2D TMD with unique nanostructures supported on CFC for excellent OER electrocatalysts.

Herein we report a facile two-step method to synthesize pyrite-type binary $Ni_{0.5}Fe_{0.5}Se_2$ nanostructures anchored on 3D CFC (Fig. 1). Firstly, electrodeposition has been used to synthesize binary NiFe hydroxides anchored on CFC. Secondly, the facile hydrothermal selenization has been applied to fabricate novel pyrite-type octahedral $Ni_{0.5}Fe_{0.5}Se_2$. The facile electrodeposition

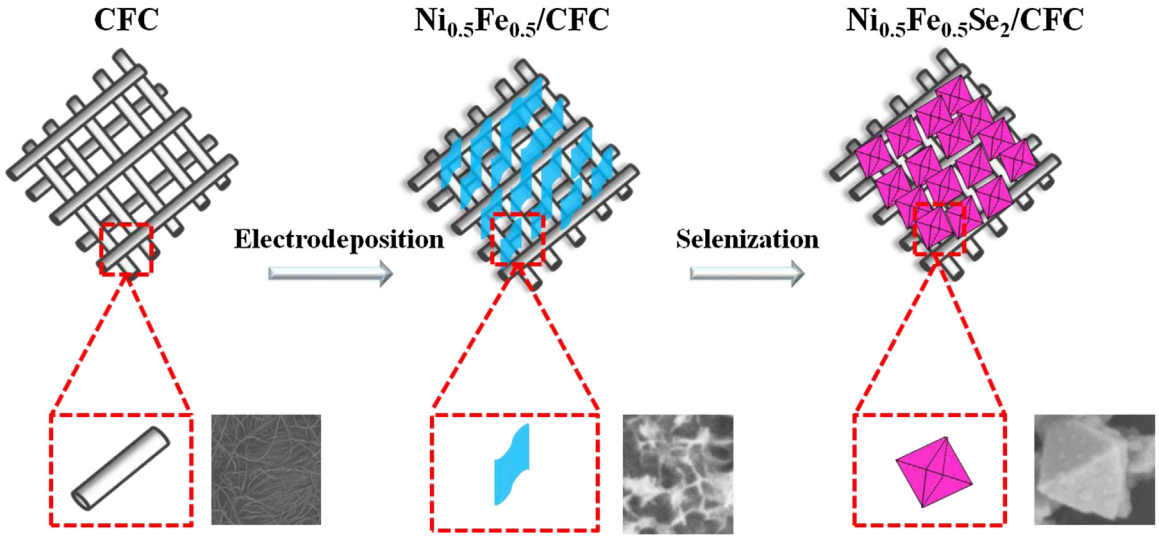

Fig. 1. Schematic illustration of the fabrication procedures for pyrite-type octahedral $Ni_{0.5}Fe_{0.5}Se_2$ on CFC.

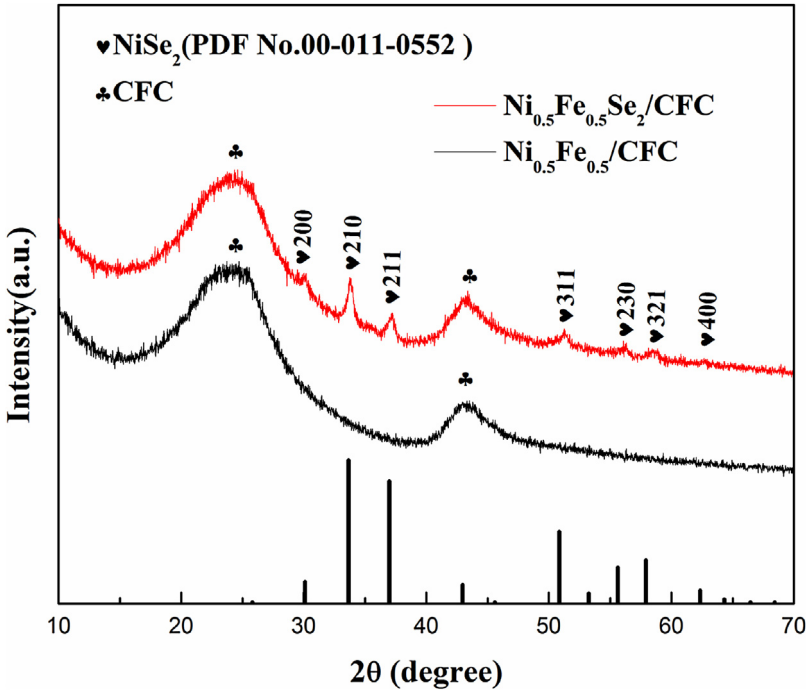

Fig. 2. XRD patterns of $Ni_{0.5}Fe_{0.5}$/CFC and $Ni_{0.5}Fe_{0.5}Se_2$/CFC.