Binder-Free Synthesis of NiCo$_2$S$_4$ Nanowires Grown on Ni Foam as an Efficient Electrocatalyst for Oxygen Evolution Reaction

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(Received March 30, 2020 : Revised March 30, 2020 : Accepted April 20, 2020)

Abstract The design and fabrication of catalysts with low-cost and high electrocatalytic activity for the oxygen evolution reaction (OER) have remained challenging because of the sluggish kinetics of this reaction. The key to the pursuit of efficient electrocatalysts is to design them with high surface area and more active sites. In this work, we have successfully synthesized a highly stable and active NiCo$_2$S$_4$ nanowire array on a Ni-foam substrate (NiCo$_2$S$_4$ NW/NF) via a two-step hydrothermal synthesis approach. This NiCo$_2$S$_4$ NW/NF exhibits overpotential as low as 275 mV, delivering a current density of 20 mA cm$^{-2}$ (versus reversible hydrogen electrode) with a low Tafel slope of 89 mV dec$^{-1}$ and superior long-term stability for 20 h in 1 M KOH electrolyte. The outstanding performance is ascribed to the inherent activity of the binder-free deposited, vertically aligned nanowire structure, which provides a large number of electrochemically active surface sites, accelerating electron transfer, and simultaneously enhancing the diffusion of electrolyte.

Key words electrocatalyst, nickel-cobalt sulfide, nanowires, hydrothermal, oxygen evolution reaction.

1. Introduction

Increasing energy demands, ever-worsening environmental pollution, and depletion of fossil fuel are stimulating the search for eco-friendly, renewable and clean energy resources for the efficient generation of energy with new methods.$^{1,2}$ Hydrogen, an ideal energy carrier considered as a promising resource to overcome the future energy crisis and meet the rising energy demands. Also, it has high energy density, excellent energy conversion efficiency and environmentally friendly nature.$^{3,4}$ Among the various methods for hydrogen production, electrochemical water splitting is regarded as a promising way to provide carbon-free and sustainable energy source of hydrogen.$^{5}$ Oxygen evolution reaction (OER) is the bottleneck in the water-splitting process due to its sluggish kinetics from the rigid O-O double bond formation and multiproton-coupled electron transfer steps. Thus, it requires high overpotential (η), even using highly active noble metal catalysts such as IrO$_2$ and RuO$_2$.$^{6-8}$ Also the scarcity and high cost of such noble metal-based catalysts always limit their large-scale industrial application. Consequently, it is of high desire to develop cost-effective, earth-abundant and highly efficient electrocatalyst for replacing the state-of-the-art precious-metal-based catalysts.$^{9,13}$

Nowadays, transition metal chalcogenides consisting of transition metal atoms (Ni, Fe, Co) and chalcogen atoms (S, Se, Te) have attracted significant attention, because of their low cost, high electrocatalytic activity, good electrical conductivity, low bandgap energy, and high stability.$^{14,15}$ Among these chalcogenides, transition metal sulfides with spinel-type AB$_2$S$_4$ structure (i.e., thiospinel, A = Ni, Co, Fe, Cu, etc.) are widely studied as compared to their corresponding oxides due to their unique redox properties and surface abundant sulfur vacancies. NiCo$_2$S$_4$ is one of the bimetallic thiospinel with a normal spinel structure furnished more octahedral catalytic active sites of Co (III) cations compared to NiCo$_2$O$_4$ with inverse spinel structure.$^{16-18}$ This helps to improve the electrochemical performance of NiCo$_2$S$_4$. It is well known that the reaction components, structural parameters, and oxidation states of cations highly influence the physicochemical properties of spinels which mostly depend on the synthesis conditions. Additionally, facile
and viable routes to synthesize NiCo$_2$S$_4$ with nanostructured morphology enhances electrocatalytic performance.$^{(9,20)}$

Herein, we report a simple and practical strategy for the fabrication of bimetallic nickel-cobalt sulfide nanowires (NiCo$_2$S$_4$ NW) on Ni-foam (NF) (labeled as NiCo$_2$S$_4$ NW/NF). This NiCo$_2$S$_4$ NW/NF electrode exhibits remarkable electrocatalytic activity for the OER, with low overpotential as 275 mV to obtain the current density of 20 mA cm$^{-2}$ in 1 M KOH electrolyte. Benefiting from the high surface area, binder-free synthesis and porous conducting NF substrate, the as-prepared NiCo$_2$S$_4$ NW/NF electrode demonstrates excellent electrocatalytic activity and long-term stability for the OER. This work will provide a new prospect for the development of electrode material for various electrochemical conversion applications.

2. Experimental

2.1 Synthesis of Nickel cobalt oxide (NiCo$_2$O$_4$/NF)

All reagents used were of analytical pure grade and used without further purification. Before synthesis, NF (1 × 1 cm) was cleaned with 1 M HCl to remove nickel oxide layers on the surface, then ultrasonicated in ethanol and water respectively for 5 min and dried in air. In a typical procedure, 1.0 mmol Nickel chloride hexahydrate (NiCl$_2$·6H$_2$O), 2.0 mmol Cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O), 6.0 mmol NH$_4$F and 15.0 mmol urea were dissolved in 35 mL distilled water and stirred to form a homogeneous solution. Then the pre-treated NF and the prepared homogeneous solution were transferred into Teflon-lined stainless-steel autoclave (100 mL). The autoclave was sealed and maintained at 120 °C for 3 h in a hot air oven and then allowed to cool to room temperature naturally. The obtained NF was then clean with distilled water and ethanol several times and then annealed at 350 °C for 2 h in air atmosphere, to obtain NiCo$_2$O$_4$/NF.

2.2 Synthesis of Nickel cobalt sulfide (NiCo$_2$S$_4$ NW/NF)

3.0 mmol Na$_2$S·9H$_2$O was dissolved in 35 mL distilled water and stirred to form a clear solution and transferred into a Teflon-lined stainless-steel autoclave (100 mL). Then the prepared NiCo$_2$O$_4$/NF was immersed into the above solution and maintained at 80 °C for 12 h and then cooled to room temperature. After the reactor was cooled to room temperature, NiCo$_2$S$_4$ NW/NF was obtained by rinsing it with distilled water and ethanol several times.

2.3 Structural characterization

The powder X-ray diffraction (XRD) measurements were recorded on a Rigaku Dmax/Ultima IV diffractometer with monochromatized Cu Kα radiation (λ = 1.54 Å). The morphology of the deposited samples was examined by field-emission scanning electron microscopes (FE-SEM, FEI Nova Nano SEM 450). X-ray photoelectron spectroscopy (XPS) measurements were recorded on a Perkin-Elmer PHI 5000C spectrometer using monochromatized Al Kα excitation. All binding energies were calibrated by using the contaminant carbon (C$_{1s}$ = 284.6 eV) as a reference.

2.4 Electrochemical measurements

All the electrochemical measurements were performed on an electrochemical workstation (CHI 760E, CH Instruments Inc., Shanghai) using a conventional three-electrode system with an electrolyte solution of 1 M KOH, a Pt wire as a counter electrode, and saturated calomel electrode (SCE) as a reference electrode and freshly prepared NiCo$_2$S$_4$ NW/NF was directly used as working electrode. All potentials measured were converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation: $E_{\text{RHE}} = E_{\text{SCE}} + (0.24 + 0.059 \text{ pH})$. Before the electrochemical measurement, the electrolyte was degassed by bubbling oxygen for at least 30 min to ensure the H$_2$O/O$_2$ equilibrium at 1.23 V (versus the RHE). Linear sweep voltammetry (LSV) was measured at the scan rate of 5 mV s$^{-1}$. The double-layer capacitance ($C_{dl}$) of the electrode was obtained by cyclic voltammetry (CV) and measured in the region of 0.20 ~ 0.25 V vs SCE with scan rates of 4, 6, 8, and 10 mV s$^{-1}$, respectively. The long-term stability was measured using chronopotentiometry at a constant current density of 20 mA cm$^{-2}$ for 20 h.

3. Results and discussion

3.1 Morphological and structural study

The morphological characterization of prepared NiCo$_2$S$_4$ film is shown in Fig. 1(a-c). Fig. 1(a) shows the low-magnification FE-SEM image of the NiCo$_2$S$_4$ NW/NF. It shows the vertically aligned NiCo$_2$S$_4$ nanowires uniformly formed on the entire NF surface. Such vertically aligned 1D nanowire structure can afford high surface area with abundant active sites. The crystal phase of NiCo$_2$S$_4$ was investigated using the XRD method. As shown in Fig. 2(a) XRD pattern reveals the crystal structure and phase purity of the NiCo$_2$S$_4$ nanowires. The strong diffraction peaks at 44.8°, 52.2°, and 76.8° are attributed to the (111), (200), and (220) planes of the NF substrate, respectively. Additionally, the peaks at 31.8°, 37.8°, 50.3°, and 55.3° are attributed to the (311), (400), (511), and (440) planes of cubic phase NiCo$_2$S$_4$ (JCPDS: 00-020-0782), respectively.$^{(17)}$

The XPS was employed to study the detailed chemical
NiCo$_2$S$_4$ Nanowires as Electrocatalyst for Oxygen Evolution Reaction

Fig. 1. FE-SEM images of NiCo$_2$S$_4$ NW/NF at different magnifications.

Fig. 2. (a) XRD patterns of NiCo$_2$S$_4$ NW/NF. XPS spectra of (b) Ni 2p, (c) Co 2p, (d) S 2p for NiCo$_2$S$_4$ NW/NF.

composition and electronic states of the NiCo$_2$S$_4$ NW/NF. Fig. 2(b) demonstrate high-resolution XPS spectrum of Ni 2p. The Ni 2p spectrum shows a pair of peaks at 855.4 eV and 872.8 eV corresponds to Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ respectively along with their satellite peaks, which confirms the existence of Ni$^{2+}$ and Ni$^{3+}$ oxidation state. For, Co 2p spectrum [Fig. 2(c)], the two main peaks Co 2p$_{3/2}$ and Co 2p$_{1/2}$ were at 781.0 and 796.1 eV respectively, which suggests the coexistence of Co$^{2+}$, Co$^{3+}$. Fig. 2(d) shows the spectrum of S 2p region, the main peak located at binding energies of 162.2 eV is attributed to the sulfur ion in low coordination at the surface. The XPS analysis clearly indicates the NiCo$_2$S$_4$ has a composition of Ni$^{2+}$, Ni$^{3+}$, Co$^{2+}$, Co$^{3+}$ and S$^{2-}$ which is in good agreement with previous reports.\(^{20}\)

3.2 Electrochemical activity towards OER

The electrocatalytic performances for the OER of as-prepared NiCo$_2$S$_4$ nanowires and NiCo$_2$O$_4$ electrocatalysts were investigated in 1 M KOH electrolyte in a typical three-electrode configuration at a scan rate of 5 mV s$^{-1}$. To understand the contribution of the NF substrate in the performance of NiCo$_2$S$_4$ NW/NF we also studied LSV of bare NF. Fig. 3(a) shows the OER polarization curves of
all electrodes and it is observed that NiCo$_2$S$_4$ NW/NF requires a low overpotential of only 275 mV to reach a current density of 20 mA cm$^{-2}$, which is much lower than that of NiCo$_2$O$_4$/NF (380 mV), and NF (410 mV) indicating the excellent catalytic performances of NiCo$_2$S$_4$ NW/NF. Tafel plots are demonstrated in Fig. 3(b). The Tafel slopes of NiCo$_2$S$_4$ NW/NF is 89 mV dec$^{-1}$, lower than that of NiCo$_2$O$_4$/NF (96 mV dec$^{-1}$) and NF (113 mV dec$^{-1}$), which means a higher electrocatalytic reaction rate and higher catalytic activity. This may be due to the faster rate of electron transfer owing to the good electrical conductivity of NiCo$_2$S$_4$ NW/NF. A comparative plot of overpotential and Tafel of three catalysts are displayed in Fig. 3(c). Besides catalytic performance, we also inspected the electrochemical durability of NiCo$_2$S$_4$ NW/NF by using chronopotentiometry. As displayed in Fig. 3(d), after 20 h of constant electrolysis at a current density of 20 mA cm$^{-2}$ there was a negligible loss in current density, demonstrating the excellent stability of the NiCo$_2$S$_4$ NW/NF. The high stability of the NiCo$_2$S$_4$ NW/NF electrode was also confirmed by the results of LSV measurements after 20 h. The LSV curves of NiCo$_2$S$_4$ NW/NF before and after stability are almost identical [inset in Fig. 4(d)].

The electrochemical double-layer capacitance (ECSA) is estimated from $C_{dl}$ where the $C_{dl}$ of catalysts was measured by simple CV tests at different scan rates of 4, 6, 8, and 10 mV s$^{-1}$ as shown in Fig. 4(a-b). In Fig. 4(c) it can be clearly seen that the $C_{dl}$ (4.36 mF cm$^{-2}$) for NiCo$_2$S$_4$ NW/NF is higher than that of NiCo$_2$O$_4$/NF (2.18 mF cm$^{-2}$). The high value of $C_{dl}$ indicates a higher electrochemically active surface area. Further, to get an insight into the OER kinetics, the electrochemical impedance analysis (EIS) was carried out. The Nyquist plots of NiCo$_2$S$_4$ NW/NF and NiCo$_2$O$_4$/NF are shown in Fig. 4(d). The Nyquist plot indicates the low charge transfer for NiCo$_2$S$_4$ NW/NF electrode than NiCo$_2$O$_4$/NF. This suggested the high electron transfer kinetics of NiCo$_2$S$_4$ NW/NF during OER. In light of all the above experimental results and analysis, we would like to attribute the enhancement in the OER activity of the NiCo$_2$S$_4$ NW/NF to several factors. (1) First of all, synergism between nickel and cobalt increases the number of their exposed active cites promotes OER activity.\(^{17}\) (2) Large S$^{2-}$ anions (than O$^{2-}$ anions) with closely packed array structure together with Ni and Co.

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**Fig. 3.** (a) OER LSV polarization curves, (b) the corresponding Tafel plots, (c) Comparative plot of overpotential and Tafel of NiCo$_2$S$_4$ NW/NF, NiCo$_2$O$_4$/NF and bare Ni-foam (d) Chronopotentiometry stability test of NiCo$_2$S4 NW/NF over 20 h at a constant current density of 20 mA cm$^{-2}$ (inset shows the polarization curve before and after the 20 h stability test).
metal cations in different valence states present in the tetrahedral and octahedral sites respectively, of the spinel crystal structure, resulting in more octahedral active sites of Co(III) cations for efficient OER activity at a very low cell voltage. (3) Vertically aligned nanowire structure of NiCo$_2$S$_4$ provides a large specific area and 3D NF substrate promotes the fast electron transfer channel. (4) Strong binding between NiCo$_2$S$_4$ nanowires and NF substrate, ensuring good electrical contact and efficient charge transfer resistance between the catalyst and the current collector.

4. Conclusion

In summary, we have successfully prepared one-dimensional NiCo$_2$S$_4$ nanowire arrays on the NF substrate via facile hydrothermal synthesis. The prepared NiCo$_2$S$_4$ electrode showed an excellent OER performance in 1 M KOH electrolyte. The NiCo$_2$S$_4$ electrode needs low overpotential of 275 mV at a current density of 20 mA cm$^{-2}$ and showing excellent stability of 20 h. ESCA and EIS analysis indicate excellent catalytic activity of the NiCo$_2$S$_4$ due to high surface area and superior reaction kinetics compared to another electrode. The uniformly grown nanowire structure of NiCo$_2$S$_4$ enhances charge transport, and highly exposed active sites. The above results demonstrate that NiCo$_2$S$_4$ NW/NF electrode is a promising, highly active and stable electrode for the OER in alkaline electrolyte conditions.

Acknowledgment

This study was financially supported by Chonnam National University (Grant number: 2017-2842).

References


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