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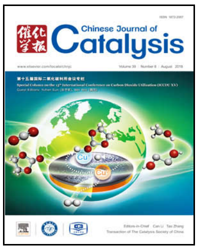

Article

Three-dimensional lily-like $CoNi_2S_4$ as an advanced bifunctional electrocatalyst for hydrogen and oxygen evolution reaction

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ABSTRACT

Designing low-cost, highly efficient, and stable bifunctional electrocatalysts for both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is of vital significance for water splitting. Herein, three-dimensional lily-like $CoNi_2S_4$ supported on nickel foam ($CoNi_2S_4$/Ni) has been fabricated by sulfuration of the Co–Ni precursor. As expected, $CoNi_2S_4$/Ni possesses such outstanding electrocatalytic properties that it requires an overpotential of only 54 mV at 10 mA cm^{-2} and 328 mV at 100 mA cm^{-2} for HER and OER, respectively. Furthermore, by utilizing the $CoNi_2S_4$/Ni electrodes as bifunctional electrocatalysts for overall water splitting, a current density of 10 mA cm^{-2} can be obtained at a voltage of only 1.56 V.

1. Introduction

Electrocatalytic splitting of water *via* hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is widely considered to be a feasible method of producing high-purity hydrogen fuel from aqueous solutions [1–3]. Nevertheless, both HER and OER require active and durable electrocatalysts to lower their overpotential and overcome sluggish kinetics [4]. To date, Pt has been regarded as the best HER electrocatalyst, while IrO_2 and RuO_2 are the most active electrocatalysts for OER [5]. Unfortunately, the scarcity and extremely high cost of these noble metals severely limit their widespread application. To this end, enormous efforts have been committed to exploring earth-abundant and inexpensive electrocatalysts, especially bifunctional electrocatalysts, for overall water splitting. These include alloys of various three-dimensional (3D) transition metals (Mn, Fe, Co, Ni, etc.) [6] and their oxides/hydroxides [7–14], sulfides [15–20], selenides [21], phosphides [22], nitrides [23], as well as carbides [17,24,25]. Among these, transition metal sulfides (TMSs), especially CoNi sulfides, have received considerable attention as they exhibit distinctive bifunctional electrocatalytic properties owing to their hydrogenase-like catalytic mechanism [26]. Liu *et al.* [27] proposed a water electrolyzer, which utilized a $NiCo_2S_4$ nanowire array on carbon cloth ($NiCo_2S_4$ NA/CC) as a bifunctional electrocatalyst in an alkaline medium, and could obtain 10 mA cm^{-2} at a cell voltage of 1.68 V. Subsequently, Fang *et al.* [28] reported that an alkaline electrolyzer based on $Ni_{2.3\%}$–CoS_2/CC only needed a cell voltage of 1.66 V to deliver 10 mA cm^{-2}. Although recent years have witnessed remarkable progress in this field of research, developing CoNi sulfides with favorable configurations for extraordinary bifunctional electrocatalytic performance remains a practical challenge.

Notably, 3D materials with unique nanostructures have

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been reported as the most promising electrocatalysts for application in electrochemical reactions due to their large surface area, fast electron transport, and abundance of active sites exposed to the electrolyte [29]. Currently, the majority of TMS-based catalysts are 1D nanowires [19,27,28] and 2D nanosheets [26]. However, these materials tend to aggregate and suffer from low electron transmission capacity, which impedes their electrocatalytic activity. Therefore, one possible solution is to develop TMS-based catalysts with distinct 3D nanostructures to obtain potential electrocatalysts for bifunctional water splitting.

Herein, we report our research on novel 3D lily-like $CoNi_2S_4$ directly grown on Ni foam ($CoNi_2S_4$/Ni). Benefiting from the active $Ni^{\delta+}$ and $S^{\delta-}$ species, large active surface area, mesoporous structure, and enhanced charge transfer capacity, the 3D lily-like $CoNi_2S_4$/Ni demonstrated excellent catalytic performance and stability toward both HER and OER in basic electrolytes. An alkaline electrolyzer assembled using this versatile $CoNi_2S_4$/Ni electrode exhibited remarkable activity for overall water splitting with 10 mA cm^{-2} at a cell voltage of only 1.56 V.

2. Experimental

2.1. Materials

$Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, CH_3CSNH_2 (Thioacetamide, TAA), CON_2H_4 (urea), and NH_4F were purchased from Aladdin. The Ni foam was purchased from Kunshan Electronic Limited Corporation. No additional purification step was performed for all the reagents.

2.2. Synthesis of the CoNi–precursor/Ni

The Ni foam (3 cm × 3 cm) was immersed in 3 mol L^{-1} HCl solution by sonication and absolute ethanol for 15 min each. Next, 0.175 g of $Co(NO_3)_2{\cdot}6H_2O$, 0.873 g of $Ni(NO_3)_2{\cdot}6H_2O$, 1.10 g of urea, and 0.10 g of NH_4F were adequately dissolved in a mixture of 30 mL of deionized water and 20 mL of absolute ethanol under agitated stirring. Next, the homogeneous solution was transferred into a Teflon-lined autoclave (80 mL) with the clean Ni foam in it. The autoclave was sealed and heated at 120 °C for 6 h. After it had cooled to ambient temperature, the CoNi–precursor/Ni was taken out and washed with deionized water thoroughly, and then dried at 60 °C for 2 h.

2.3. Synthesis of the $CoNi_2S_4$/Ni

The as-prepared CoNi–precursor/Ni was added to 50 mL deionized water with 0.376 g TAA, and the mixture was stirred to form a homogeneous solution. The resulting solution was transferred into an autoclave and heated at 160 °C for 4 h. Upon cooling to room temperature spontaneously, the as-made material was washed thrice with deionized water and ethanol to remove impurities on the surface, and then dried at 60 °C overnight. The mass loading of $CoNi_2S_4$/Ni is 3.8 mg cm^{-2}.

2.4. Characterization

The X-ray diffraction (XRD) pattern was obtained from a MSAL-XD2 X-ray diffractometer with Cu Ka radiation (λ = 1.5406 Å). Scanning electron microscopy (SEM) images were obtained from a Philips SEM-XL30S microscope operated at 15 kV. High-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) coupled with an energy-dispersive X-ray spectroscopy (EDS) analyzer was conducted at an accelerating voltage of 200 kV. Inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out on PerkinElmer Optima 2000DV. Nitrogen sorption isotherm was tested by a Micromeritics TriStar 3000 analyzer at –196 °C. The X-ray photoelectron spectroscopy (XPS) measurements were analyzed by an ESCALab 250.

2.5. Electrochemical measurements

Electrochemical measurements were performed in a standard three-electrode system in which the as-prepared samples, Pt foil, and Hg/HgO electrodes served as the working, counter, and reference electrodes, respectively. The electrolyte was 1.0 mol L^{-1} KOH solution. All potentials were converted *via* the Nernst equation ($E_{RHE} = E_{Hg/Hg_2Cl_2} + (0.059\ pH + 0.242)$ V). The polarization curves were obtained by linear sweep voltammetry (LSV) at a scan rate of 1 mV s^{-1}. The overpotentials (η) were computed according to the equation ($\eta = E_{RHE} - 1.23$ V). Electrochemical impedance spectroscopy (EIS) measurements were analyzed in the frequency range of 10 kHz to 10 mHz with an amplitude of 5 mV. Chronoamperometric tests were conducted at given potentials.

3. Results and discussion

As schematically illustrated in Fig. 1, the 3D lily-like $CoNi_2S_4$/Ni was synthesized *via* sulfuration of the CoNi–precursor/Ni. Similar to a previous report [15], the XRD patterns of $CoNi_2S_4$/Ni and CoNi–precursor/Ni were tested using their powders scraped down from the Ni foam. The XRD pattern of the CoNi–precursor in Fig. 2(a) reveals that the peaks at 11.6°, 23.3°, 34.9°, 39.5°, 46.9°, 60.9°, and 62.3° are derived from $(Ni_{6.10}Co_{2.90})(OH)_{18.27}(CO_3)_{1.315}{\cdot}6.7H_2O$ (JCPDS no. 33–0429), while the other peaks at 17.5° and 36.5° correspond to $Co(CO_3)_{0.5}(OH){\cdot}0.11H_2O$ (JCPDS no. 48–0083). Therefore, we name this mixture precursor as CoNi–C–Co–CHH. After sulfuration, the diffraction peaks of CoNi–C–Co–CHH are not ob-

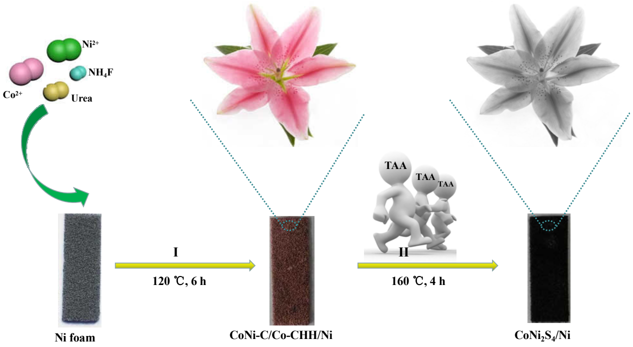

Fig. 1. Schematic illustration of the fabrication of lily-like $CoNi_2S_4$/Ni.