



Redox route to ultrathin metal sulfides nanosheet arrays-anchored MnO₂ nanoparticles as self-supported electrocatalysts for efficient water splitting

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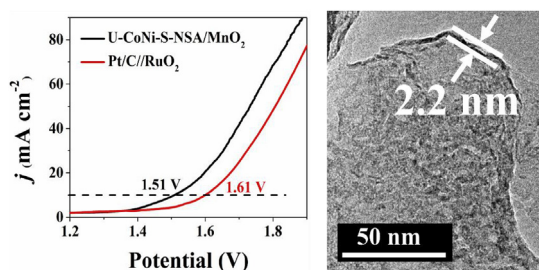
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HIGHLIGHTS

- Ultrathin CoNi-sulfides nanosheet arrays-anchored MnO₂ nanoparticles are crafted.
- The hierarchical arrays provide abundant active sites for electrocatalysis.
- Kinetics advantages are demonstrated on the hierarchically porous architecture.
- The nanocomposites display outstanding performance for overall water splitting.

GRAPHICAL ABSTRACT



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ABSTRACT

The efficient and sustainable production of high-purity hydrogen gas through electrochemical water splitting calls for robust and bifunctional catalysts to accelerate the two half reactions of water splitting. Herein, we *in-situ* craft ultrathin CoNi-sulfides nanosheet (~ 2.2 nm in thickness) arrays-anchored MnO₂ nanoparticles (~ 3.2 nm in diameter) (denoted U-CoNi-S-NSA/MnO₂) via a spontaneous redox process between CoNi-sulfides nanosheet and MnO₄⁻ anions at ambient temperature. The hierarchical U-CoNi-S-NSA/MnO₂ nanocomposites are then directly employed as self-supported catalysts for the two half reactions of water splitting, showing excellent activity with small overpotentials of 170 mV for oxygen evolution reaction and 67 mV for hydrogen evolution reaction to achieve 10 mA cm⁻², respectively. Moreover, an efficient water electrolyzer through using U-CoNi-S-NSA/MnO₂ as both anodic and cathodic catalysts is fabricated, which achieves current density of 10 mA cm⁻² at a small voltage of 1.51 V over a long-time operation of 20 h. This outstanding performance is markedly superior than that of precious Pt/C//RuO₂ counterpart (1.61 V). Therefore, the as-synthesized hierarchical nanocomposites are promising candidates for cheap and efficient water splitting.

1. Introduction

Hydrogen has been widely recognized as a green and effective energy resource to substitute for non-renewable fossil fuels. Electrochemical water splitting is a promising route to generate hydrogen (H₂) from earth-abundant water (H₂O) by using renewable energy resource (i.e. solar energy, wind) [1–4]. Unfortunately, such water

splitting is a thermodynamically adverse process with large overpotentials required for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) to reach appreciable reaction rate [5–8]. Recently, Ru/Ir-based [9] and Pt-based [10] electrocatalysts have shown satisfying activity for OER and HER, respectively. Nevertheless, the high-cost and scarcity of precious metals (i.e. Ru, Ir and Pt) make their further commercial application impractical. Clearly, in terms of

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environmental and economical sustainability, it is very attractive to fabricate efficient catalysts based on earth-abundant elements for electrochemical water splitting. In this regard, transition metal sulfides (TMS) (i.e. NiS₂, NiCo₂S₄, Co₉S₈ and MoS₂) [11–14] were developed as robust catalysts for OER and/or HER because of the combined advantages of high abundance, low-cost, and high activity. However, most reported TMS are powder materials or compacted films [15,16], which often lead to the insufficient exposure of active centers and poor electron transport inside the bulk components of TMS.

Recently, ultrathin two-dimensional (2D) layered materials have provoked enormous interest in the electrocatalysis field due to their dramatically improved surface/volume ratio and unique electronic structures, which grant the exposure of more active centers [17–19]. For example, ultrathin 2D MnO₂ nanosheets containing abundant oxygen vacancies showed excellent performance for both of OER and HER [20]. Furthermore, directly growing self-supported 2D nanosheet arrays on the conductive substrates (i.e. nickel foams [21] and carbon clothes [22]) without binders can markedly improve conductivity of the arrays and facilitate the electron transfer during electrocatalytic processes. Therefore, to efficiently utilize the intriguing features of TMS, it is highly imperative to rationally engineer an ultrathin nanosheet arrays-grown on Ni foams with sophisticated nanoarchitectures, affording more accessibly active centers and superior conductivity.

Herein, we reported the design and crafting of an ultrathin CoNi-sulfides nanosheet (~2.2 nm in thickness) arrays-anchored MnO₂ nanoparticles (NPs) (~3.2 nm in diameter) (denoted U-CoNi-S-NSA/MnO₂) grown on Ni foams by a spontaneous redox process on the CoNi-sulfides nanosheet arrays (denoted CoNi-S-NSA) at ambient temperature. Intriguingly, we found that the thickness of CoNi-sulfides nanosheet could be markedly reduced to form ultrathin sulfides nanosheets by the oxidation etching of MnO₄⁻ anions, and meanwhile the MnO₂ NPs were uniformly anchored on the ultrathin CoNi-sulfides nanosheet by the reduction of MnO₄⁻ anions. Consequently, with abundant active centers exposed on both ultrathin CoNi-sulfides nanosheets and MnO₂ NPs, the fast transport of electron and mass in the hierarchical nanostructure, the U-CoNi-S-NSA/MnO₂ catalyst exhibited excellent performance on both OER and HER. Notably, the excellent U-CoNi-S-NSA/MnO₂ could be applied as both cathodic and anodic electrocatalysts to yield a water-splitting current density of 10 mA cm⁻² at voltage of 1.51 V with outstanding stability of 20 h, outperforming of reported non-precious metal-based electrolyzers and the precious Pt/C//RuO₂ electrolyzer. This work demonstrated a new bottom-up approach for the facile preparation of hierarchical nanocomposites for efficiently electrocatalytic processes.

2. Experimental section

2.1. Electrocatalysts synthesis

2.1.1. Synthesis of CoNi-layered double hydroxide (CoNi-LDH) nanosheet arrays (denoted CoNi-LDH-NSA)

The CoNi-LDH nanosheet arrays were grown on the Ni foams through a hydrothermal coprecipitation method [23]. Typically, Ni(NO₃)₂·6H₂O (2 mmol), Co(NO₃)₂·6H₂O (4 mmol), NH₄F (10 mmol), and hexamethylenetetramine (30 mmol) were dissolved in distilled water (60 ml) and stirred to generate a solution A. Then, a piece of Ni foam (3 cm × 5 cm) was cleaned with 2 M HCl solution, distilled water, and absolute ethanol (each for 10 min) in an ultrasound bath to ensure a well-cleaned surface. Afterward, the Ni foam and solution A were transferred into a 100 ml autoclave, which was heated to 110 °C for 12 h and then cooled to ambient temperature naturally. Finally, the resulting green Ni foam was rinsed with distilled water and absolute ethanol (each for 5 min), and dried at 70 °C for 12 h. For comparison, the CoNi-LDH-NSA-1 and CoNi-LDH-NSA-3 (1 and 3 refer to the molar ratio of Co²⁺/Ni²⁺) were also prepared through the same process as that of CoNi-LDH-NSA except that the added Co(NO₃)₂·6H₂O changed to

2 mmol and 6 mmol, respectively. The Ni-hydroxides nanosheet arrays (denoted Ni-OH-NSA) without Co elements were also prepared through the same process as that of CoNi-LDH-NSA but without adding Co(NO₃)₂·6H₂O.

2.1.2. Synthesis of CoNi-sulfides nanosheet arrays (denoted CoNi-S-NSA)

The CoNi-sulfides nanosheet arrays were synthesized by a hydrothermal vulcanization process of the CoNi-LDH-NSA precursor. In a typical synthesis, the thioacetamide (0.06 g) was first dissolved in distilled water (60 ml) to generate a solution B. And then, the solution B and as-synthesized CoNi-LDH-NSA were transferred into a 100 ml autoclave, which was heated to 140 °C for 6 h and then cooled to ambient temperature. Finally, the resulting black Ni foam was rinsed with distilled water and absolute ethanol (each for 5 min), which was dried at 70 °C for 12 h. The CoNi-S-NSA-1, CoNi-S-NSA-3, and Ni-S-NSA were also synthesized as the process of CoNi-S-NSA but changing the CoNi-LDH-NSA precursor to CoNi-LDH-NSA-1, CoNi-LDH-NSA-3, and Ni-OH-NSA.

2.1.3. Synthesis of ultrathin-CoNi-sulfides nanosheet arrays-anchored MnO₂ NPs (denoted U-CoNi-S-NSA/MnO₂)

The ultrathin-CoNi-sulfides nanosheet arrays-anchored MnO₂ NPs were *in-situ* synthesized by treatment of CoNi-S-NSA with potassium permanganate (KMnO₄) solution at ambient temperature. First, the KMnO₄ (0.95 g) was dissolved in distilled water (60 ml) to form a clear solution C. And then, the as-synthesized CoNi-S-NSA was immersed into the solution C at ambient temperature for 30 min. Finally, the resulting black Ni foam was rinsed with absolute ethanol for 10 min, which was dried at 70 °C for 12 h. The U-CoNi-S-NSA-1/MnO₂, U-CoNi-S-NSA-3/MnO₂, and U-Ni-S-NSA/MnO₂ were also synthesized as controlled samples through the same procedure of that U-CoNi-S-NSA/MnO₂ except changing the CoNi-S-NSA to CoNi-S-NSA-1, CoNi-S-NSA-3, and Ni-S-NSA. To investigate the role of MnO₂ for OER and HER, the MnO₂ species were selectively etched from U-CoNi-S-NSA/MnO₂ through immersing it in 0.5 M H₂SO₄ solution for 24 h. The obtained product denoted U-CoNi-S-NSA.

2.2. Characterizations

X-ray diffraction (XRD) data of as-synthesized samples was recorded using a D8ADVANCE diffractometer over a 2θ range of 5–70°. Field emission scanning electron microscopy (FESEM) were performed on a JEOL JSM-7800F. Transmission electron microscopy (TEM) and corresponding high-resolution TEM (HRTEM) images were obtained on a JEOL 2100 electron microscope using an acceleration voltage of 200 kV. HAADF-STEM-EDS studies were conducted over a JEM-2100F instrument with an EDS system. The low-temperature N₂ adsorption-desorption experiments were conducted over a Micromeritics ASAP 2020 sorptometer to investigate the pore structure of samples. X-ray photoelectron spectroscopy (XPS) of different samples were studied on a Thermo VG ESCALAB250 X-ray photoelectron spectrometer with AlK_α X-ray radiation. The thickness of CoNi-sulfides nanosheets was measured on a Dimension Icon (Bruker Corporation) through atomic force microscopy (AFM).

2.3. Electrochemical characterizations

The performance of as-synthesized arrays towards HER and OER was evaluated on an electrochemical workstation (CHI 760 E) using 1 M KOH solution as electrolyte. All electrochemical tests were performed on a three-electrode system, in which catalysts (i.e. CoNi-LDH-NSA, CoNi-S-NSA, U-CoNi-S-NSA/MnO₂) supported Ni foams (1 cm × 1 cm) served as working electrodes, carbon electrodes worked as counter electrodes, Hg/HgO electrodes (in 1 M KOH) applied as reference electrodes. The electrochemical impedance spectroscopy (EIS) of OER was performed from 1 MHz to 1 Hz at potential of 1.43 V. The cycling

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