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ACo₂O₄ (A=Ni, Zn, Mn) nanostructure arrays grown on nickel foam as efficient electrocatalysts for oxygen evolution reaction

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ABSTRACT

Developing highly efficient, low-cost and superior stable electrocatalysts for the oxygen evolution reaction (OER) is essential for coping with global energy shortage and environmental crisis. In this article, ACo₂O₄/NF (A = Mn, Zn, Ni) composites were synthesized via a facile hydrothermal and calcination method and used as electrocatalytic water oxidation catalysts. The hybrid structure, chemical composition, oxidation state and surface morphology of ACo₂O₄/NF (A = Mn, Zn, Ni) has been confirmed by powder X-ray diffraction (XRD), energy dispersive X-ray (EDX), X-ray photoelectron (XPS), scanning electron microscopy (SEM), transmission Electron Microscope (TEM) and Brunauer-Emmett-Teller (BET) analysis. Such self-supported NiCo₂O₄/NF hybrid shows a smaller overpotential of 271 mV at current density of 10 mA cm⁻² in 1 M KOH, which is comparable to most reported NiCo₂O₄ materials (monomer or composite) for OER. Influence on catalytic activity of doping different metal ions in ACo₂O₄/NF was investigated systematically for the first time. Improved electrocatalytic activity of NiCo₂O₄/NF is attributed to the special homogeneous urchin-like structure and porous property.

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Introduction

Due to the high abundance, low weight, large energy density and environment friendliness, hydrogen has attracted considerable attention and used as an ideal energy alternative to fossil fuels [1–5]. Benefiting from abundant water resources on earth, electrocatalytic hydrogen evolution reaction is deemed to be a practical and promising strategy to produce hydrogen efficiently [6–9]. In general, water splitting is

composed of two distinct parts: anodic oxygen evolution reaction (OER) [10–12] and cathodic hydrogen evolution reaction (HER) [13–16]. The OER involved with four electrons process is one of the key processes for water splitting, but bottleneck of curb mass production of hydrogen is that high overpotential of OER always leads to great energy loss [17]. Rational utilization of high efficiency catalyst is considered as an excellent approach to reduce overpotential [18]. To date, RuO₂ and IrO₂ still remain the highest electrocatalytic activity for OER, but

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low storage, high cost and poor stability confine their large-scale applications [19,20]. It is urgent to efficiently and facilely synthesis low-cost new catalytic materials with high activity, low over-potential and long-term stability to replace noble metal-based catalysts.

In recent years, tremendous efforts have been dedicated to develop superactive noble-metal-free OER catalysts based on plentiful metals (Co [21], Ni [22], Zn [23], and Mn [24], etc) and ACo_2O_4 has aroused widespread concern owing to their excellent conductivity and superior electrochemical activity [25,26]. Numerous studies reveal that 3d transition metal oxides of ACo_2O_4 appear spinel structure, which is built around a cubic closely packed array of O^{2-} ions with A^{2+} occupying one-eighth of tetrahedral sites and Co^{3+} cations occupying half of the octahedral sites [27]. The spinel structures contain unique electroactive solid-state redox couples of $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{A}^{3+}/\text{A}^{2+}$. These redox pairs will greatly beneficial for electrochemical energy storage and conversion applications [28]. Therefore, ACo_2O_4 stands out as a splendid electrode material for OER. For example, Su et al. reported a spinal NiCo_2O_4 nanowire arrays with lager surface area and outstanding conductivity, which processes remarkable catalytic activity compared to single Co_3O_4 and NiO [29].

OER performance of electrode materials is closely linked with mass transportation and electron conduction [30–32]. Large surface area of fine particles always leads to fast electron conduction rate but aggregation of particles also reduce conductivity [33]. In order to obtain materials with large specific surface area and choiceness conductivity, nanoarrays such as carbon nanotubes [34], stainless steel mesh [35], graphene [36] and nickel foam [37] were applied to electron materials because of their special structure with more pores and notable mass transportation. For example, Rao et al. reported NiCo_2O_4 hexagonal nanoplates grown on reduced graphene oxide sheets by a facile two-step solution phase, which showed higher oxidation peak currents and smaller onset potential than the individual NiCo_2O_4 [38]. The unique opening structure, three-dimensional mesh, inherent tensile strength and thermal shock resistance made nickel foam widely used in electrode material and catalyst preparation [39–41]. Herein, ACo_2O_4 (Ni, Mn, Zn)/NF composites were synthesized via facile hydrothermal and calcination approach, and influence on catalytic activity of doping with different metal ions was investigated systematically for the first time. Results demonstrated that $\text{NiCo}_2\text{O}_4/\text{NF}$ composite exhibits the best electrochemical catalytic activity by comparing overpotential, Tafel slope, and impedance for OER.

Experimental

Materials

All the chemicals used in the experiment were of analytical grade and used without further purification. Water used throughout all experiments was purified through a Molecular Lab water purification system. Nickel Foam was purchased from Shenzhen Green and Creative Environmental Science and Technology Co. Ltd.

Synthesis of $\text{NiCo}_2\text{O}_4/\text{NF}$

Nickel foams were dipped into 3 M HCl solution for 5 min to remove any impurities and oxide layer. Then NF substrates were ultrasonicated in ethanol, acetone and deionized water consecutively for 15 min, followed by drying in vacuum at 60 °C for 8 h. NF substrates were pressed to 1 mm thickness and cut into 3 cm × 8 cm squares for deposition. 2.5 mmol nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), 5 mmol cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and 12 mmol urea were mixed together in 50 mL deionized water and then stirred for 10 min to obtain a clear solution. The reaction solution together with as-prepared NFs were then transferred into a 100 ml autoclave, and maintained at 150 °C for 6 h in an electric oven. After cooling down to room temperature naturally, the resultant composite was washed several times with ethanol, DI water respectively and then dried in air. Finally, the composite was annealed at 300 °C for 2 h in air environment with a heating rate of 5 °C min^{-1} to obtain $\text{NiCo}_2\text{O}_4/\text{NF}$.

Synthesis of $\text{MnCo}_2\text{O}_4/\text{NF}$

$\text{MnCo}_2\text{O}_4/\text{NF}$ was synthesized according to the procedure that of $\text{NiCo}_2\text{O}_4/\text{NF}$, except that nickel chloride hexahydrate was substituted by manganese chloride tetrahydrate.

Synthesis of $\text{ZnCo}_2\text{O}_4/\text{NF}$

Synthesis procedure of $\text{ZnCo}_2\text{O}_4/\text{NF}$ was also similar to $\text{NiCo}_2\text{O}_4/\text{NF}$, except that nickel chloride hexahydrate was substituted by zinc chloride.

Materials characterization

The crystallographic information and phase compositions were obtained by X-ray diffraction (XRD, Bruker D8 ADVANCE diffractometer, $\lambda = 1.5418 \text{ \AA}$). The elemental composition and valence state of constituted elements were investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Al Ka, 150 W). Surface morphology and elemental composition were investigated by scanning electron microscopy (SEM, Hitachi S-5200), X-ray energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM, Tecnai F20). BET surface area was measured using a Micromeritics Instrument corporation sorption analyzer (TriSta II 3020).

Electrochemical measurements

All electrochemical analyses were carried out with a computer-controlled CHI 660E electrochemical workstation in a conventional three-electrode system using $\text{ACo}_2\text{O}_4/\text{NF}$ (A = Ni, Zn, Mn) as working electrode, a platinum wire electrode as counter electrode and an Ag/AgCl electrode as reference electrode at room temperature. The catalytic activity was measured via linear sweep voltammetry (LSV) at a scan rate of 5 mV/s in 1 M KOH solution. Electrochemical impedance spectroscopy (EIS) measurements were recorded at open-circuit potential in the frequency range of 100 kHz to 100 mHz. Chronoamperometric measurements were tested on corresponding potential to support a current density of

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