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Short Communication

CuCo₂O₄ microflowers catalyst with oxygen evolution activity comparable to that of noble metal

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ABSTRACT

It is of high significance to design efficient, low-cost and durable electrocatalysts for the reaction (OER) in alkaline solution. In this communication, we report the development of CuCo₂O₄ microflowers directly on nickel foam (CuCo₂O₄/NF) as an efficient and durable electrocatalyst for OER. Such CuCo₂O₄/NF demands overpotential of only 296 mV to drive a geometrical catalytic current density of 20 mA cm⁻², 73 mV and 145 mV less than that for Co₃O₄/NF and NF, respectively, which are better than that of RuO₂/NF. Furthermore, CuCo₂O₄/NF presents an excellent long-term electrochemical durability maintaining the activity at overpotential of 240 mV for 10 h.

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Introduction

Owing to the increasing energy consumption and environmental pollution, developing clean renewable energy to substitute the fossil fuel is of great significance [1–21,26]. Electrochemical water splitting provides a facile method to the large-scale production of clean hydrogen in the future. However, suffering from complex multi-electron transfer processes and sluggish kinetics, the oxygen evolution reaction (OER) performance become the main limitation to improve the efficiency of water splitting [22,23]. Noble metal oxides like RuO₂ [24] and IrO₂ are the most active OER electrocatalysts, but

the high cost, poor stability and scarcity limit their widespread applications. Therefore, developing earth abundant, high efficiency and excellent stability OER catalyst is highly desirable. In this regard, cobalt-based electrocatalysts have been extensively investigated as efficient catalyst owing to the low overpotential, high current densities and environmentally friendly. Additionally, there is a widespread concern on spinel cobaltites catalyst especially for binary spinel cobaltites, such as M_xCo_{3-x}O₄, (M = Ni²⁺, Mn²⁺, Zn²⁺ and Cu²⁺) [25]. Among these OER catalysts, the Ni_xCo_{3-x}O₄ have been studied as efficient OER catalysts because of their large number of available active sites and multiple valences oxidation states. However, CuCo₂O₄ exhibited relatively poor water oxidation

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activity and stability in the previously reported literature. Many research groups do their best to improve water oxidation activity of CuCo_2O_4 through various methods. Papakonstantinou [26] et al. reported that $\text{CuCo}_2\text{O}_4/\text{NrGO}$ catalyst exhibited a current density of 10 mA cm^{-2} at a small overpotential of 360 mV in 1 M KOH and concluded that the enhanced OER performance of $\text{CuCo}_2\text{O}_4/\text{NrGO}$ is attributed to the presence of Cu^{2+} ions at the octahedral sites, reduction in the size of the CuCo_2O_4 nanoparticles, enhancement of electrochemically active surface area, and synergetic effect between CuCo_2O_4 nanoparticles and NrGO sheets. Srivastava [27] et al. noted that $\text{Cu}_{0.3}\text{Co}_{2.7}\text{O}_4$ nanochains demonstrated low overpotential ($\sim 351 \text{ mV}$) and good cycling stability (1000 cycles) in strong alkaline media. Zheng [28] et al. reported that the CuCo Hybrid Oxides could catalyze both HER and OER and reach a 10 mA cm^{-2} overall water splitting current at 1.61 V. However, the activity and stability of OER for CuCo_2O_4 need to be improved further even the massive efforts have been made by the research groups. In addition, $\text{CuCo}_2\text{O}_4/\text{NF}$ microflowers heterostructures have not been reported as efficient electrocatalysts for water oxidation to date.

In this communication, CuCo_2O_4 microflowers on nickel foam ($\text{CuCo}_2\text{O}_4/\text{NF}$) were firstly synthesized via a simple hydrothermal and calcination process. As a 3D OER electrode in 1.0 M KOH (pH = 13.6), $\text{CuCo}_2\text{O}_4/\text{NF}$ exhibits superior catalytic activity with the overpotential of 296 mV to reach a

geometrical catalytic current density of 20 mA cm^{-2} , which is superior to the RuO_2/NF , $\text{Co}_3\text{O}_4/\text{NF}$ and NF. Additionally, the $\text{CuCo}_2\text{O}_4/\text{NF}$ electrocatalyst shows the good durability and high catalytic activity without degradation for 10 h.

Results and discussion

The X-ray diffraction (XRD) pattern for $\text{CuCo}_2\text{O}_4/\text{NF}$ (Fig. 1a) shows five obvious characteristic peaks at 31.18° , 36.74° , 55.49° , 59.18° and 65.04° indexed to the (220), (311), (422), (333) and (440) plans of CuCo_2O_4 (JCPDS no. 37-0878), respectively. Three obvious peaks at 44.6° , 52.0° and 76.6° are observed from the XRD pattern of $\text{CuCo}_2\text{O}_4/\text{NF}$, which are originated from the Nickel foam (JCPDS no. 70-0989). Co_3O_4 nanoneedles array on the Ni foam are also prepared hydrothermally and the XRD peaks at $2\theta = 19^\circ$, 31.27° , 36.85° , 59.36° and 65.23° are assigned to the (111), (220), (311), (551) and (440) plans of Co_3O_4 (JCPDS No. 42-1467) (Fig. S1).

To investigate the surface morphology and structure of the as-prepared $\text{CuCo}_2\text{O}_4/\text{NF}$ and $\text{Co}_3\text{O}_4/\text{NF}$, scanning electron microscopy (SEM) images of products are performed in Fig. 1b–d. It is obviously showed that $\text{CuCo}_2\text{O}_4/\text{NF}$ and $\text{Co}_3\text{O}_4/\text{NF}$ are uniformly and homogeneously covering on the nickel foam skeletons. Fig. 1d reveals that needle-like Co_3O_4 with a smooth surface is dense grown on the surface of Ni foam.

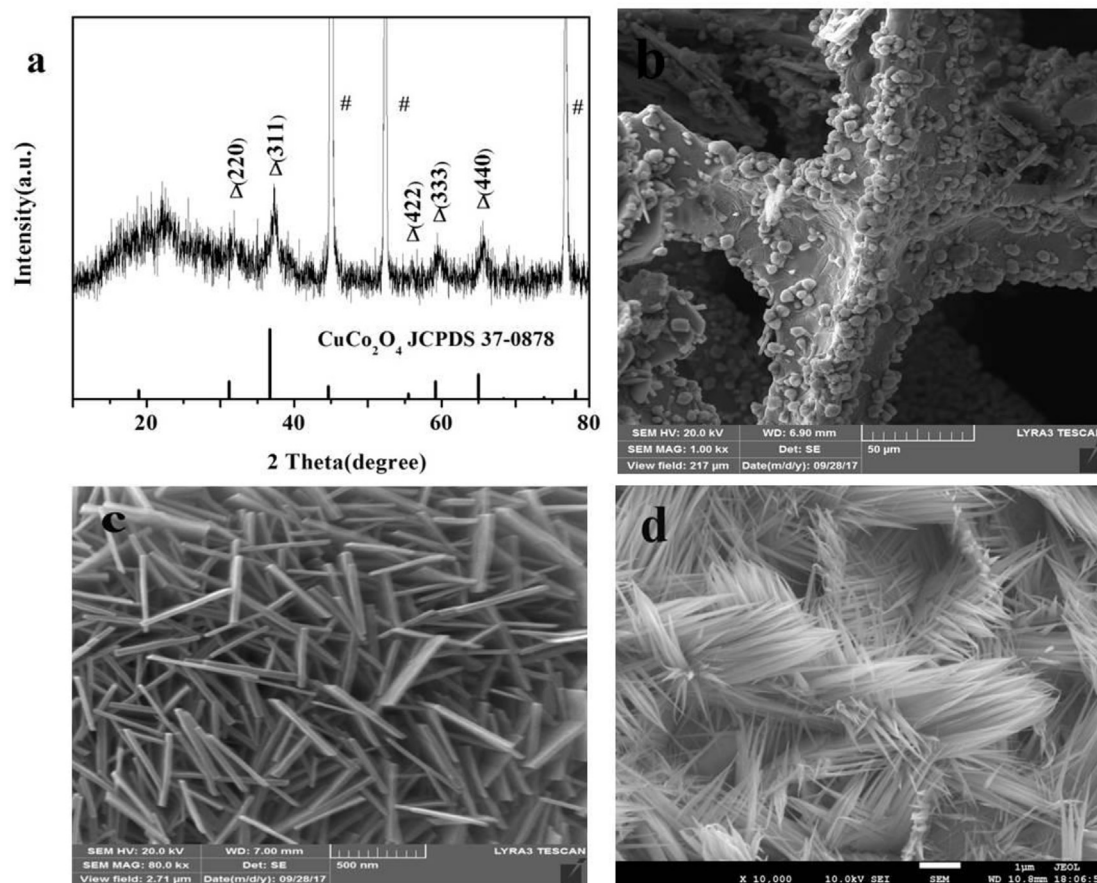


Fig. 1 – The XRD patterns of $\text{CuCo}_2\text{O}_4/\text{NF}$ (a). SEM images of the as-obtained $\text{CuCo}_2\text{O}_4/\text{NF}$ (b, c) and $\text{Co}_3\text{O}_4/\text{NF}$ (d).

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