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Constructing self-standing and non-precious metal heterogeneous nanowire arrays as high-performance oxygen evolution electrocatalysts: Beyond the electronegativity effect of the substrate



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HIGHLIGHTS

- The role of the substrate for the OER is investigated.
- The OER activity is related to the synergistic effect between catalyst and substrate.
- DFT calculations reveal a compromised adsorption energy by combining Fe and Co.
- An active and robust CuO@CoFeO_x self-standing nanowire OER catalyst is constructed.

ARTICLE INFO	A B S T R A C T
Keywords: Oxygen evolution reaction Cobalt iron oxides Nanowire arrays Substrates Adsorption energy	Self-standing nanowires are the focus of intense interest as oxygen evolution reaction catalysts due to their natural advantages. However, the role of the substrate used for self-standing nanowires in oxygen evolution reaction is not fully investigated. Herein, we report that the oxygen evolution reaction activity is closely associated with the substrate. The oxygen evolution reaction activity of cobalt oxide catalysts is enhanced with the increasing electronegativity of the substrates, while iron oxide catalysts break this rule due to the stronger synergistic interplay between iron and copper compared to that between iron and gold. Under the guidance of these findings, we construct a highly active and robust non-precious-metal $CuO@CoFeO_x$ self-standing nanowire electrocatalyst, which shows a constant current density of 10 mA cm ⁻² at an overpotential of 0.36 V for 300 h continuously without noticeable degradation in 0.1 M KOH solution. Moreover, the $CuO@CoFeO_x$ nanowire anode coupled with a Pt-Ni foam cathode shows an attractive overpotential of 0.39 V to provide a current density of 10 mA cm ⁻² for water electrolysis in 1.0 M KOH solution.

1. Introduction

Growing concerns about environmental pollution and increasing demands for energy have motivated the search for clean and renewable energy sources [1]. The oxygen evolution reaction (OER) is a key step in many energy conversion and storage devices, such as water electrolysers and metal-air batteries. This critical step occurs via the reaction $40H^- \rightarrow O_2 + 2H_2O + 4e^-$ in basic solution. However, it always needs a large overpotential (η) to reach a desirable current density due to the sluggish kinetics involved [2,3]. Noble metal oxides, such as

 RuO_2 and IrO_2 , are the most active electrocatalysts for OER [4]. However, limited abundance, high cost and poor stability have inevitably hindered their practical application. Thus, developing lowcost, earth-abundant and durable electrocatalysts with high catalytic activity for OER is critically important [5].

Self-standing nanowires have been considered as a new generation of advanced OER electrodes and show several advantages over powdery catalysts [6]. First, nanowires directly grown onto the surface of conductive substrates ensures the participation of each nanowire in the reaction and thus enables their direct usage as working electrodes [7].

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Second, they eliminate the need for a conductive (carbon) or binder (e.g., Nafion^{*}) additive component that can contribute to or hinder OER activity [8]. Finally, the large surface area of nanowires can provide an abundance of active sites while the open space between individual nanowires can facilitate the diffusion of reactants and products, which can increase the OER current density [9]. Considerable efforts have been devoted to exploiting efficient self-standing nanowire electrocatalysts, but most have focused on developing highly active species with a random conductive substrate.

For a long time, substrates have been merely regarded as conductive current collectors for self-standing nanowire electrodes. The effect of substrates on the active species is rarely investigated. Recent work has demonstrated that the OER activity of CoO_x depends on the electronegativity of the substrate (including Au, Pt, Pd, Cu and Co substrates) [10]. It shows the highest OER activity on Au substrates due to the high electronegativity of Au among all metals [10]. However, noble metals (such as Au, Pt and Pd) are not suitable for large scale use because their usage as the substrate material runs against the original intention of developing earth-abundant, low-cost electrocatalysts. Therefore, there is tremendous interest in the substitution of the Au substrate with a noble-metal-free substrate that can show a comparable enhancement of the OER performance.

Here, we designed a self-standing CuO nanowire (CuO NW) electrode with large surface area and high electronegativity on top of a Cu substrate, which enhanced the OER activity of cobalt-iron active species compared to a monolithic Cu substrate and even an Au substrate. A significant finding is that substrates not only act as conductive current collectors but also influence the performance of the active species depending on the electronegativity and the synergistic effect between substrate and the active species. Moreover, the distinct self-standing nanowire morphology provided sufficient active sites to reduce the overpotential. The control of the electronegativity of the substrate and the synergistic effect between Cu. Co and Fe elements enabled one to tune the electronic structure to further enhance the OER activity and stability. Consequently, we showed that the CuO@CoFeOx catalyst can provide a current density of 10 mA cm⁻² at an overpotential of 0.36 V that is stable for over 300 h without noticeable attenuation. Therefore, this study demonstrates a facile approach to fabricate an easy to scaleup and cost-effective OER catalyst.

2. Experimental

2.1. Preparation

2.1.1. Preparation of CuO NWs

First, $Cu(OH)_2$ NWs were prepared by a solution oxidation method. In a typical procedure, Cu foils were cleaned in an aqueous 3.0 M HCl solution for 5 min, followed by repeated rinsing with distilled water (DI-water). Cu foil (3*3 cm) was placed into a mixed solution (8 g NaOH and 2.282 g NH₄S₂O₄ in 75 mL deionized water) for 8 min. Then the resulted product was rinsed with ethanol and DI-water several times. The obtained blue film covered on the Cu foil surface is Cu(OH)₂. The CuO NWs were converted from Cu(OH)₂ NWs after being heated overnight in air at 200 °C. The CuO coated Cu substrates were synthesized by reducing the NH₄S₂O₄ to 0.228 g. The other conditions are the same as the synthesize routes for CuO NWs. The acid washed Cu foil was used as Cu substrate.

2.1.2. Preparation of elcetrocatalysts

 CoO_x and FeO_x thin-films were prepared by magnetron sputtering at 40 W power on two sides of Cu foils, Au substrates, CuO coated Cu substrates and CuO NWs with a base pressure of 10^{-3} Pa via argon (Ar) and oxygen (O₂) with a ratio of 4:1 atm under 350 °C. The targets were Co and Fe metal (purity: 99.999%). CoFeO_x were prepared by Co-sputtering Co and Fe targets. The other conditions were the same as those for sputtering individual CoO_x and FeO_x thin-films. The thickness

of these three thin-films were the same.

2.2. Characterizations

X-ray diffraction patterns were obtained on a Rigaku Smartlab by continuous scanning in the 20 range of 10–60° with an interval of 0.02°. The transition metal oxidation states were detected by X-ray photoelectron spectroscopy (PHI5000 Versaprobe spectrometer). The surface morphology of catalysts was detected by a field emission scanning electron microscope (Hitachi S-4800). The transmission electron microscopy images and HAADF-STEM and the corresponding EDS spectroscopy element mapping were taken on an FEI Tecnai G2 F30 STWIN field-emission transmission electron microscope. Inductively coupled plasma-mass spectroscopy was performed with a Varian Vista-Pro instrument to determine the compositions of oxides. The thickness information was evaluated by a film thickness detector system which based by the principle of quartz crystal oscillation.

2.3. Measurement of mass loading

The mass loading was detected by a 9 MHz quartz crystal microbalance instrument (Princeton Applied Research QCM922). Please see Ref. [3] for the detailed information. Based on above calculations, the mass loadings of CoO_x , FeO_x and $CoFeO_x$ on the Au substrates are 19.35, 17.46 and $18.08 \,\mu g \, cm^{-2}$, respectively. The mass loadings of these active species are nearly identical. In addition, the mass loading of RuO_x is $20.84 \,\mu g \, cm^{-2}$.

2.4. Electrochemical measurements

Electrochemical measurements were conducted in a three-electrode electrochemical cell comprising of a working electrode, a platinum wire counter electrode and an Ag|AgCl (3.5 M KCl) reference electrode connected to a SP-300 workstation at room temperature. The area of working electrodes was 0.2 cm^2 . The electrolyte was bubbled with oxygen for about half an hour before the start of each measurement. Cyclic voltammetry curves were performed at a constant scan rate of 10 mV s^{-1} from 1.13 to 1.93 V, which was calibrated to the reversible hydrogen electrode (RHE) (0.95 V in 0.1 M KOH solution).

2.5. DFT calculations

The adsorption of OH on the (001) crystal surface of Co_3O_4 , α -Fe₂O₃ and γ -Fe₂O₃ and on the (100) crystal surface of FeO were computed through density functional theory (DFT) method. The $Co_3O_4(001)$ surface has the energetically preferred termination [11]. The α -Fe₂O₃(001) is the low-index surface showing catalytic oxidation activity [12]. The γ -Fe₂O₃(001) is predicted for the growth morphology which possesses catalytic activity [13]. The FeO(100) is the facet normally used to study the adsorption of ORR-OER intermediates theoretically [14]. The Fe doped Co₃O₄(001) surface was built through substituting one Co atom by one Fe atom. The surfaces were constructed from the optimized bulk phases. The cleaved surface was firstly geometrically optimized by relaxing all atoms. Then the OH was put on the surface and further optimization was proceeded. Several layers of bottom atoms were frozen in this procedure. The single point calculation was performed on the optimized adsorption system to obtain the energetic information.

All DFT calculations were performed using the Amsterdam Density Functional (ADF) package (version 2017). The revised Perdew-Burke-Ernzerhof (revPBE) functional [15] within the generalized gradient approximation (GGA) was applied to deal with the electron exchangecorrelation [16]. The Grimme's correction employing BJ-damping (-D3(BJ)) [17] was used to account for the dispersion interaction. The atomic orbitals with double-zeta quality and one polarization function (DZP) [18] was adopted. The relativistic effects of heavy atoms were taken into account by employing the scalar zero order regular Download English Version:

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