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Strongly coupling of Co_9S_8/Zn-Co-S heterostructures rooted in carbon nanocages towards efficient oxygen evolution reaction

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ABSTRACT

The design of efficient and nonprecious electrocatalysts towards oxygen evolution reaction (OER) is extremely essential for a wide range of renewable energy technologies but remains a grand challenge. Herein, a novel hybrid composite constructed from Co_9S_8/Co-doped ZnS ($Zn_{0.8}Co_{0.2}S$) nanorods with the atomic-level coupled nanointerface rooted in porous carbon polyhedra ($Co_9S_8/Zn_{0.8}Co_{0.2}S@C$) have been fabricated and investigated as a highly efficient electrocatalyst for OER. The composite catalyst can afford a current density of 10 mA cm^{-2} at a low overpotential of only 292 mV and a small Tafel slope of $\sim$52 mV $decade^{-1}$, which are superior to the state-of-the-art IrO_2/C and most reported Co-based catalysts. Experimental and computational studies reveal an electronic coupling between Co_9S_8 and $Zn_{0.8}Co_{0.2}S$ that can facilitate the electron injection from the electrode and transport to the active site, and thus generates a favorable local coordination environment and greatly enhances the OER process.

1. Introduction

Electrochemical water splitting represents one of the most appealing strategies to convert intermittent energy into chemical fuels, *i.e.* hydrogen and oxygen [1–5]. As an important half-reaction involved, oxygen evolution reaction (OER) is the bottleneck of the overall water splitting process owing to the sluggish four-proton-coupled electron transfer and high activation energy for the formation of O=O double bond [6–9]. Efficient electrocatalysts are of great significance to drive the reaction in terms of reducing the overpotential and improving the reaction kinetics. To date, noble metal-based catalysts such as IrO_2 and RuO_2 are considered as the most active electrocatalysts for OER [10,11], but their scarcity and high cost seriously hampered practical applications on a large scale. Accordingly, considerable efforts have been devoted to designing and synthesizing efficient but inexpensive OER electrocatalysts based on earth-abundant materials [12–23]. As an alternative to noble-metal catalysts, *3d* transition metal chalcogenides that contain Fe, Co, Ni or their mixtures have emerged as competent electrocatalyst for OER due to their good catalytic activity, low cost and environmental friendliness [24–28]. Nevertheless, the use of metal chalcogenide electrocatalyst is still limited by their low intrinsic electrical conductivity and easy self-agglomeration [29], which in most cases lead to a high overpotential and decreased reaction rate.

Several approaches have been proposed to further improve the OER catalytic performance of the transition metal chalcogenides. One effective approach is the introduction of additional metals to form mixed metal chalcogenides with unchanged matrix properties that can modulate the electronic structure and enhance the energetics for OER, usually outperforming their single-component counterparts. For example, Xia et al. reported that $(Ni, Co)_{0.85}Se$ nanoarrays exhibited higher OER catalytic activity than the single $Co_{0.85}Se$ nanoarrays [30]. Jiang et al. demonstrated that ternary $FeNiS_2$ nanosheets could deliver better electrocatalytic performance compared to the corresponding FeS and Ni_9S_8 nanosheets [31]. Another attractive approach is the optimization of the morphology and structure of metal chalcogenides to increase the active catalytic sites and, meanwhile, facilitate mass transportation during OER. As revealed by Cai et al., oxygen-containing ultrafine cobalt sulfide with hollow structure as OER catalyst could expose more active sites and thus showed great advantages over the bulk cobalt sulfide catalyst [32]. Liu et al. found that $CoSe_2$ ultrathin nanosheets with atomic thickness could efficiently catalyze the OER with low overpotential of 0.32 V, significantly lower than 0.59 V for the bulk $CoSe_2$ [33]. Moreover, combining the metal chalcogenides with conductive carbonaceous matrix to enhance the conductivity and charge transfer of the whole system have also

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been proven to remarkably improve the performance of OER catalyst [34–37]. Despite these impressive advances made recently, the rational design of highly efficient metal chalcogenides-based OER catalyst is still a big challenge.

Bearing these points in mind, herein we have integrated all three of the above individual approaches into one and designed a complex metal chalcogenides-based composites, in which heterostructures consisting of ultrafine Co_9S_8 nanoparticles and Co-doped ZnS ($Zn_{0.8}Co_{0.2}S$) nanorods with atomic-level coupled interface rooted in N-doped porous hollow carbon polyhedra (denoted as $Co_9S_8/Zn_{0.8}Co_{0.2}S$@C). The composites catalyst can be prepared using a convenient and low-cost zeolitic imidazolate frameworks (ZIFs)-engaged method and exhibits one of the highest OER activities among known Co-based catalysts. By means of combined experimental and theoretical investigations, it is proposed that the strong electronic interactions between Co_9S_8 and $Zn_{0.8}Co_{0.2}S$ in the heterostructures can reduce the free energy of the oxygen-containing intermediates and thus promote the catalytic reactions.

2. Experimental

2.1. Preparation of bimetallic Zn-Co-ZIF precursor

In a typical preparation, 0.5 mmol zinc nitrate hexahydrate and 0.5 mmol cobalt nitrate hexahydrate were dissolved in 25 ml methanol. The solution was thoroughly mixed by stirring 1 h. Then, the as-obtained solution was slowly injected into 25 ml methanol solution containing 1.66 g of 2-methylimidazole (1 mmol). After about 30 min vigorously stirred, the mixture was placed at room temperature for 24 h. The resulting purple precipitates (Zn-Co-ZIF) were centrifuged and washed with ethanol for at least three times, and finally dried in a vacuum at 70 °C.

2.2. Synthesis of $Zn_{0.8}Co_{0.2}S/Co_9S_8$@C composite

The as-obtained Zn-Co-ZIF and S powders were mixed with a weight ratio of 1:2 in a quartz crucible, which was then loaded within a tube furnace. To maintain the original morphology, the mixture was firstly heated to 300 °C at a ramping rate of 2 °C min^{-1} and kept at this temperature for 1 h. Then, the samples were heated to 650 °C at a ramping rate of 2 °C min^{-1} and kept at this target temperature for 2 h under a flow nitrogen gas. After naturally cooling down to 25 °C, the $Zn_{0.8}Co_{0.2}S/Co_9S_8$@C powders with black color were obtained. For comparison, ZnS@C, $Zn_{0.8}Co_{0.2}S$@C, and Co_9S_8@C composites were synthesized by a process similar to that for making $Zn_{0.8}Co_{0.2}S/Co_9S_8$@C but using different molar ratios between zinc nitrate hexahydrate and cobalt nitrate hexahydrate (Table S1). To estimate the carbon content in the composite, 200 mg of $Zn_{0.8}Co_{0.2}S/Co_9S_8$@C were firstly stirred with HCl solution at 50 °C for 48 h to remove the Zn and Co species. After that, about 16 mg of final products, *i.e.*, carbon matrix, were obtained by centrifugation with ethanol for several times followed by drying at 60 °C for 12 h in vacuum. Thus, it can be known that the C content in the composite is about 8 wt%.

2.3. Preparation of a physical mixture of $Zn_{0.8}Co_{0.2}S$@C and Co_9S_8@C, and IrO_2@C

The physical mixture of $Zn_{0.8}Co_{0.2}S$@C and Co_9S_8@C was obtained by hand-milling 63 wt% of $Zn_{0.8}Co_{0.2}S$@C and 37 of wt.% Co_9S_8@C for 1 h. The IrO_2@C mixture was obtained by hand-milling 90 wt% of IrO_2 and 10 wt% of Super-P carbon black for 1 h.

2.4. Materials characterizations

To investigate the phase structures, powder X-ray diffraction (XRD) measurements were carried out on a D8 ADVANCE X-ray diffractometer with Cu Kα radiation (0.02° $step^{-1}$, 1 s $step^{-1}$); the XRD patterns were refined by using the Rietveld program RIETAN-2000 [38]. During the refinement, we have applied the Brindley correction, the pseudo-Voigt function containing a Lorentzian part and a Gaussian part, as well as the linear constraint for occupation factors of the Zn and Co atoms in crystal structure. To assess the quality of refinement for each XRD pattern, the reliability factors R_p (R-pattern) and R_{wp} (R-weighted pattern) as well as the goodness of fit S were provided. Field-emission scanning electron microscope (FESEM, JEOL JSM-6700F) and transmission electron microscope (TEM, JEOL JEM-2100F) were used to examine the morphology and microstructure of the obtained products, respectively. The specific surface area (SSA) of samples was measured on ASAP 2020 Plus HD88 instrument. Raman spectroscopy was recorded to acquire the carbon structure by using Renishaw via plus laser Raman spectrometer. XPS measurements were performed on a Kratos XSAM-800 spectrometer with a Mg Kα radiation source. A monochromatic Al Kα1 X-ray (hγ = 1486.6 eV) implemented with a SPECS PHOIBOS 150 electron energy analyzer (total energy resolution: 0.50 eV) was conducted to acquire high-resolution XPS. A polycrystalline Ag foil was used to calibrate the binding energy.

2.5. Preparation of working electrodes

To prepare the working electrodes, powder samples (5 mg) were firstly dispersed in ethanol (976 μL), followed by the addition of Dupont Nafion 117 solution (24 μL, 5 wt%). Followed that, the mixed solution was sonicated for 30 min to obtain a homogeneous catalyst suspension. Finally, 8 μL of catalyst suspension was cast onto the surface of glass carbon (GC) electrode with a 3 mm diameter, and the working electrode was naturally dried at 25 °C before electrochemical measurements.

2.6. Electrochemical measurements

All measurements were conducted in a three-electrode cell with an Autolab electrochemical workstation (PGSTAT 302N) at 25 °C in the O_2 saturated 0.1 M KOH solution for OER. A saturated calomel electrode (SCE) and a carbon rod were used as the reference electrode and the counter electrode, respectively. Linear sweep voltammetry (LSV) was measured in the alkaline solution at a scan rate of 10 mV s^{-1}. All potentials were carried out to compensate for the ohmic potential drop losses (R_s) that induced by the solution resistance and calibrated with respect to reversible hydrogen electrode (RHE) based on following equation $E_{vs.RHE} = E_{vs.SCE} + 0.2412 + 0.05916pH - iR_s$. On the basis of the LSV, turnover frequencies (TOF) was calculated based on the previously reported work [39] (Detail calculation was provided in the S2, supporting information). To estimate the apparent electrochemical double layer capacitance (C_{dl}), cyclic voltammetry (CV) was conducted at non-Faradaic region. The electrochemical impedance spectra (EIS) was tested in a frequency range of 100 kHz–0.01 Hz at the potential 0.6 V vs. RHE (alternating current voltage at a 10 mV amplitude). The cycle durability tests were carried out by the chronoamperometric response at 0.60 V in the O_2 saturated 0.1 M KOH solution.

2.7. Theoretical calculations

The first-principle calculations were performed with the Vienna ab initio software package (VASP) [40]. The projector augmented-wave (PAW) method is employed to describe the wavefunctions