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Three-dimensional coral-like cobalt selenide as an advanced electrocatalyst for highly efficient oxygen evolution reaction

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ABSTRACT

Oxygen evolution reaction (OER) influences some important renewable energy technologies such as water splitting. Although many OER electrocatalysts have been studied to surmount this difficult problem, the development of a highly active, inexpensive and sustained OER electrocatalyst is still a great challenge. In this study, we report a novel, cost-effective cobalt selenide (coral-like CoSe) electrocatalyst with high current density (~97.5 mA cm^{-2} at 1.606 V vs. RHE) and strong durability in alkaline media. The chronoamperometric response of coral-like CoSe electrocatalyst can remain 98% of its initial current density after 10000 s at the overpotential of 350 mV in 1 M KOH. The prepared coral-like CoSe electrode exhibits a low overpotential of 295 mV at a current density of 10 mA cm^{-2} and a small Tafel slope of 40 mV dec^{-1}, which exceeds previously reported state-of-art RuO_2 electrocatalyst and is much better than CoSe nanoparticles (CoSe NPs) and precursor $Co(OH)_2$ electrocatalysts. This work affords us a 3D Co-based electrocatalyst with high performance and strong durability under alkaline conditions, which can be applied to energy conversion and storage processes.

1. Introduction

With the growing global demand for clean and sustainable energy, oxygen electrochemistry has been widely researched in recent years [1–3]. OER, as the process of generating molecular oxygen through electrochemical oxidation of water, is crucial for the development of energy conversion and storage processes, such as rechargeable metal-air batteries, water-splitting and solar fuel production [4–7]. However, the kinetics of water oxidation to oxygen is slow because it involves a 4-electron transfer process ($4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ in alkaline condition, $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ in acidic condition) to form one molecular oxygen, where serious overpotential is required [8–11]. Therefore, we need a stable and high performance electrocatalyst so as to lower the large overpotential and accelerate the OER. Although noble metal oxides, for instance, RuO_2 and IrO_2 are thought to be the most active OER electrocatalysts with low overpotentials and high current densities in both acidic and alkaline solutions [12,13], they are not appropriate for global scale applications because they are scarce and expensive [14]. Currently, researchers have made great effort to search for highly active materials which are abundant on earth based on not only non-noble transition metals like Mn, Fe, Co, Ni, but non-metal OER electrocatalysts, for instance, molecular electrocatalysts [15], chalcogenides [16], phosphates [17], borides [18], nitrides [19], transition metals and their oxides (hydroxides) [20–23], perovskites[24] and N-active materials[25] to replace the scarce and expensive noble metals (Ru and Ir). However, the performance of most developed low-cost transition metal and non-metal electrocatalysts are still inferior to the Ru and Ir standard. As a result, developing highly efficient electrocatalysts is extremely urgent.

It is well known that transition-metal chalcogenides have prominent electronic structures and physical appearance, for instance, excellent conductivity, magnetic property and half-metallicity [26–28]. First-row transition-metal dichalcogenides, especially $CoSe_2$, have been consumingly probed as hopeful catalysts for the oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), OER and photocatalytic water oxidation. For example, Feng et al. researched the electrocatalytic activity of $CoSe_2$ nanoparticles supported on carbon for ORR [29]. Kong et al. exploited an efficient and durable HER electrocatalyst of $CoSe_2$ grown on carbon fiber paper, which is capable of driving large cathodic current at low overpotential and steadily function over a long period of time [30]. Liu et al. developed a remarkable and

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earth-abundant OER electrocatalyst based on ultrathin $CoSe_2$ nanosheets, which can efficiently catalyze the OER with small Tafel slopes, low overpotential and large turnover frequencies [31]. Zhang et al. found that $CoSe_2$ can decorate visible light photocatalysts. Because of the accelerated charge carrier transfer rate and reduced overpotential, all modified semiconductors display much enhanced photocatalytic water oxidation activities [32]. The information above forecasted that $CoSe_2$ is a very promising electrocatalyst amongst the ones based on non-noble metals. Moreover, Co and Se are cheap and plentiful on earth, as the sources for $CoSe_2$. Two phases for cobalt selenides are stable at room temperature, known as CoSe and $CoSe_2$. However, the investigation of OER activity of CoSe has rarely been reported, although there are several applications of CoSe in the ORR and HER fields [33,34].

Herein, we report an OER electrocatalyst of coral-like CoSe prepared by two-step solvothermal reaction fabrication. It is found that the as-synthesized coral-like CoSe reveals highly efficient performance and good catalytic stability as an OER electrocatalyst. In 1 M KOH, the coral-like CoSe electrocatalyst affords a low overpotential of 295 mV at a current density of 10 mA cm^{-2} and a small Tafel slope of 40 mV dec^{-1}. Such good OER performance is better than that of the state-of-the-art RuO_2 electrocatalyst, which displays that the coral-like CoSe is very promising among OER electrocatalysts and have a potential to replace the expensively commercial catalysts such as RuO_2.

2. Experimental details

2.1. Materials

Polyethylene-polypropylene glycol was obtained from Energy Chemical (China). Absolute ethanol, cobalt nitrate hexahydrate, hexamethylenetetramine, ethylene glycol, Se powder, sodium borohydride and sodium hydroxide were purchased from Chengdu Kelong Chemical Co., Ltd (China). Nafion solution (5%) was provided by Shanghai Hesen Electrical Co., Ltd (China). All chemicals were used without further purification.

2.2. Synthesis of precursor flower-like $Co(OH)_2$

The flower-like $Co(OH)_2$ was prepared using a modified solvothermal reaction method similar to previous literature [35]. In a typical procedure, 0.2 g of polyethylene-polypropylene glycol (Pluronic P123) was added into mixture of 13 g of absolute ethanol and 1 g of double-distilled water under vigorous stirring for 20 min to form a transparent solution. Then 0.5 mmol of Co $(NO)_3{\cdot}6H_2O$ and 0.5 mmol of hexamethylenetetramine were added into the solution above. After stirring for 10 min, a pink solution was obtained. Sequentially, 13 mL of ethylene glycol was poured into the ethanol solution and kept stirring for another 30 min to form a clear solution. The obtained precursor solution was statically aged for 1 day before transferred into two 20 mL autoclaves and then heated at 170 °C for 2 h. After cooling down to room temperature, the product was washed and centrifuged with double-distilled water and absolute ethanol for several times before dried in vacuum oven at 60 °C for 24 h to get celadon powders of the precursor.

2.3. Synthesis of coral-like CoSe

The coral-like CoSe was prepared following a gentle and widespread anion exchange mechanism [36] involving anion exchange of $Co(OH)_2$ with selenide ions by a solvothermal reaction method. Typically, 0.1 mmol of $Co(OH)_2$ precursor was added into 12 mL of double-distilled water in a beaker under magnetic stirring for 30 min to form a homogeneous solution. Then 0.1 mmol of Se powder was dispersed in the above solution under intense stirring for 30 min before 0.3 mmol of $NaBH_4$ was added into the mixture under continuous stirring for another 1 h. Later on, the mixture was transferred into a 20 mL autoclave and heated at 180 °C for 15 h. After cooling down to room temperature, the product was washed with double-distilled water and absolute ethanol and centrifuged for several times. The black powder was then collected and dried in vacuum oven at 60 °C for 24 h, named as coral-like CoSe.

2.4. Synthesis of CoSe NPs

For the purpose of comparison, CoSe NPs were prepared using $Co(NO)_3{\cdot}6H_2O$ as precursor by only one step solvothermal reaction method, which is similar to the second step of synthesis of coral-like CoSe. The product was named as CoSe NPs.

2.5. Materials Characterizations

Different analytical techniques were applied to characterize these samples. Wide angle X-ray powder diffraction (XRD) was carried out on a Tongda TD-3500 X-ray powder diffractometer (Liaoning, China) with Cu-Kα radiation (α=0.15148 nm) operating at 30.0 kV and 20.0 mA. Small angle XRD pattern of coral-like CoSe was collected on an X-ray diffractometer (X'PERT PRO MPD DY129, Holland). Scanning electron microscopy (SEM) images were obtained from a Hitachi S4800 scanning electron microscope (Tokyo, Japan). Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) were measured by a Hitachi H-800 microscope operating at 200 kV (Tokyo, Japan). The X-ray photoelectron spectra (XPS) were acquired using a Kratos XSAM 800 spectrometer (Manchester, U.K.) with Mg-Ka X-ray (1253.6 eV) excitation source running at 15.0 kV, a hemi-spherical electron energy analyzer and a multichannel detector. The Brunauer-Emmett-Teller (BET) specific surface area and pore size distribution were achieved from the nitrogen (N_2) adsorption method using a Quantachrome NOVA 1000e apparatus automated gas sorption system.

2.6. Electrocatalytic study

Electrochemical experiments were conducted in a standard three-electrode glass cell using an electrode of glassy carbon (GC, 3 mm diameter, 0.07 cm^2) connected to an Autolab PGSTAT 302 electrochemical workstation (Eco Chemie B.V., Amsterdam, the Netherlands) to collect data at room temperature (25 °C). The GC electrode was polished to mirror finish by 0.3 micron alumina suspension then 0.05 micron suspension on a polishing cloth, and thoroughly cleaned before used as the working electrode. Platinum plate and Hg/HgO electrode were used as counter and reference electrodes, respectively. The potentials reported in our work were converted to the reversible hydrogen electrode (RHE), where in 1 M KOH, $E(RHE) = E(Hg/HgO) + 0.92$ V. The equation of $\eta(V) = E(RHE) - E_\theta$ was used to calculate overpotentials of these electrocatalysts, where E_θ represents the thermodynamic potential for OER (1.23 V vs. RHE) [37].

The preparation method of the working electrodes was as follows: In brief, 5 mg of electrocatalyst powder was dispersed in 375 μL water and 125 μL isopropanol before 10 μL of Nafion solution was added to the solution. The mixture was ultrasonicated for about 1 h to form a homogeneous ink. 2 μL of the electrocatalyst ink was transferred onto a fresh GC electrode afterwards, leading to an electrocatalyst loading of ~0.28 mg cm^{-2}. Finally, the as-prepared electrocatalyst film was dried at room temperature.