



Template-assisted synthesis of hierarchically porous Co_3O_4 with enhanced oxygen evolution activity[☆]

Lan Yao ^{a,b}, Hexiang Zhong ^{a,*}, Chengwei Deng ^{a,b}, Xianfeng Li ^{a,c}, Huamin Zhang ^{a,c,**}

^a Division of Energy Storage, Dalian National Laboratory for Clean Energy (DNL), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

^b Graduate University of the Chinese Academy of Sciences, Beijing 100049, China

^c Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), Dalian 116023, Liaoning, China

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ABSTRACT

Oxygen evolution reaction (OER) is one of the most important reactions in the energy storage devices such as metal-air batteries and unitized regenerative fuel cells (URFCs). However, the kinetically sluggishness of OER and the high prices as well as the scarcity of the most active precious metal electrocatalysts are the major bottleneck in these devices. Developing low-cost non-precious metal catalysts with high activity and stability for OER is highly desirable. A facile, in situ template method combining the dodecyl benzene sulfonic acid sodium (SDBS) assisted hydrothermal process with subsequent high-temperature treatment was developed to prepare porous Co_3O_4 with improved surface area and hierarchical porous structure as precious catalysts alternative for oxygen evolution reaction (OER). Due to the unique structure, the as-prepared catalyst shows higher electrocatalytic activity than Co_3O_4 prepared by traditional thermal-decomposition method (noted as $\text{Co}_3\text{O}_4\text{-T}$) and commercial IrO_2 catalyst for OER in 0.1 M KOH aqueous solution. Moreover, it displays improved stability than $\text{Co}_3\text{O}_4\text{-T}$. The results demonstrate a highly efficient, scalable, and low cost method for developing highly active and stable OER electrocatalysts in alkaline solutions.

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1. Introduction

With global concerns about shortage of fossil fuels and environmental pollution issues, the development of sustainable energy storage devices such as metal-air batteries and unitized regenerative fuel cells (URFCs) has been urgently required [1,2]. In the fields, the efficient oxygen evolution reaction (OER) is of crucial importance and possesses continued challenges [3,4]. However, the high overpotential of OER constrains the efficiencies of these devices [5,6]. Therefore, it is critical to develop the high-performance and cost-effective catalysts for oxygen evolution through water splitting either electrochemically or photoelectrochemically. Generally, OER occurs at a potential which most metal surfaces are oxidized and form an oxide layer, indicating that metal oxide can be the most

suitable catalysts. Although precious metal oxides, such as RuO_2 [7] and IrO_2 [8], are considered as the most active OER electrocatalysts, they are not suitable for large-scale applications because of their scarcity and high costs. Therefore, the exploration of non-precious OER electrocatalysts with high activity and stability is significantly demanded.

Extensive research efforts have been focused on developing low cost alternative materials of precious metal catalysts including organometallic compounds, transition metal oxides such as Fe_3O_4 [9], MnO_2 [10], Co_3O_4 [11,12], and NiCo_2O_4 [13,14]. Among these non-precious metal catalysts, Co_3O_4 has been considered as one of the most promising electrocatalyst for OER due to their high catalytic activity, good stability as well as low cost [15–18]. Various synthesis methods have been explored to prepare Co_3O_4 with controlled nanostructures and construct novel energy-storage devices with excellent performances such as hydrothermal precipitation [19], electrodeposition [20], thermal decomposition [21–23]. Among these methods, the hydrothermal method is widely applied due to the easily controllable parameters, mild reaction temperature and simple equipment as well as low cost [24]. However, because of the large surface energy, metal oxide nanoparticles are easily aggregated during the synthesis process, which results in the decrease of their surface area and negative impact on their catalytic activity. Although significant improvements have been achieved, the activity and stability of

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* Corresponding author. Tel: +86 411 84379935; Fax: +86 411 84665057.

** Corresponding author. Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), Dalian 116023, Liaoning, China.

E-mail addresses: zhonghexiang@dicp.ac.cn (H. Zhong), [\(H. Zhang\).](mailto:zhanghm@dicp.ac.cn)

the Co_3O_4 catalyst still cannot meet the requirement of scalable practical application due to their low surface area.

Many articles proved that the high specific surface area is beneficial for the activity of Co_3O_4 catalysts [18,25]. Poizot et al. [26] suggested that there was an optimum particle size for each metal oxide and hence the best electrochemical performance. However, the Co_3O_4 catalysts synthesized with the traditional method easily agglomerate and form large particles. Therefore, it is highly desirable to develop an efficient method for the synthesis of monodisperse nanoparticles for catalytic applications.

Herein, a facile, *in situ* template method combining the dodecyl benzene sulfonic acid sodium (SDBS) assisted hydrothermal process with high-temperature treatment was developed to prepare hierarchically porous Co_3O_4 . The as prepared catalysts, noted as Co_3O_4 -S are with small particle size, improved surface area as well as hierarchically porous structure favoring OER. It displays excellent electrocatalytic activity toward OER, which is higher than those of Co_3O_4 -T catalyst and commercial IrO_2/C catalyst in 0.1 M KOH aqueous solution. Moreover, it also presents superior stability, indicating the possibility as a promising catalyst candidate for OER. The results demonstrate the surface area, pore structure and crystalline size of the resulting porous nano particles can significantly affect its catalytic activity.

2. Experimental

2.1. Synthesis of Co_3O_4 nanoparticles

All the reagents in this experiment were of analytical purity and used as received without further purification. The Co_3O_4 were synthesized through the hydrothermal self-assembly of Co^{2+} and SDBS, combining with the following thermal treatment of the resulting precursor in air to remove organic component to form porous Co_3O_4 directly. The detailed process is as follows: 0.70 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1.0 g (2.9 mmol) of SDBS ($\text{C}_{18}\text{H}_{29}\text{SO}_3\text{Na}$) were dissolved in 20 mL deionized water under magnetic stirring, obtaining an opaque lavender blush suspension. The obtained suspension was subsequently transferred into a 100 mL Teflon-lined stainless steel autoclave. Then the autoclave was sealed and maintained at 180 °C for 5 h, and subsequently cooled down to room temperature. The obtained lilaceous precipitates were centrifuged and rinsed with deionized water and ethanol for several times to remove any alkaline salt and surfactant. Finally, the precipitates were dried under vacuum at 70 °C for 2 h and then annealed at 500 °C for 2 h with a ramping rate of 3 °C/min to obtain the final product Co_3O_4 nanoparticles. The Co_3O_4 (Co_3O_4 -T) synthesized by the thermal decomposition of precursors was taken as a comparison.

2.2. Characterizations

X-ray diffraction (XRD) spectra were measured on a PANalytical X'Pert PRO powder X-ray diffractometer operating at 40 kV and 30 mA with $\text{Cu K}\alpha$ ($\lambda = 0.15405$ nm) as a radiation source. Data were collected in a 2θ range of 10°–90° with an increment of 0.05° and a measuring time of 1 min per step.

N_2 absorption/desorption measurements were conducted on a Micromeritics ASAP 2020 physisorption analyzer to characterize the surface area and pore structure of the catalysts. Brunauer–Emmett–Teller (BET) models were used to calculate the specific surface areas. Pore size distributions (PSDs) were determined from the desorption branch of the isotherms based on the Barrett–Joyner–Halenda (BJH) method. Before the test, the samples were degassed at 300 °C for 10 h under vacuum.

Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-2000EX (120 kV) microscope. The samples were

ultrasonically dispersed in ethanol and dropped onto a holey carbon film on a copper grid.

X-ray photoelectron spectra (XPS) were carried out on an ESCALAB 250 (Thermo Scientific) XPS spectrometer with an Al $K\alpha$ excitation sources (1486.6 eV). The binding energies obtained in the XPS analyses were corrected by the C 1s line at 284.6 eV from adventitious carbon.

2.3. Electrochemical measurements

The electrocatalytic activities and stabilities of the samples were evaluated by the electrochemical measurements with a CHI600 potentiostat in a three-electrode electrochemical cell. An Hg/HgO electrode and a graphite rod were utilized as the reference and counter electrodes, respectively. In this study, all potentials were referred to the reversible hydrogen electrode (RHE). The working electrode was the thin film coated glass carbon electrode prepared with the as-prepared catalyst. Carbon powder (Vulcan XC-72) was added with mass loading of 40 wt% into the oxide powder to conduct the electrocatalytic measurement and Nafion was used as a binder. The detailed fabrication process was as follows: 5 mg of the catalyst with the catalysts loading of 60 wt% and 50 μL 5 wt% Nafion solution (Dupont, USA) were ultrasonically dispersed in 1 mL iso-propanol to form homogeneous ink. Then 10 μL of the catalyst ink was cast onto a glass carbon electrode of 4 mm in diameter as the working electrode. Cyclic voltammetry (CV) was performed ranging from 0.8 to 1.5 V at a scan rate of 50 mV/s using nitrogen-saturated 0.1 M KOH electrolyte solutions. The OER activity of the catalysts was evaluated using the rotating disk electrode (RDE) in 0.1 M KOH with linear sweep voltammetry (LSV) from 1.1 V to 1.9 V at a scan rate of 5 mV/s at a rotating speed of 1600 rpm.

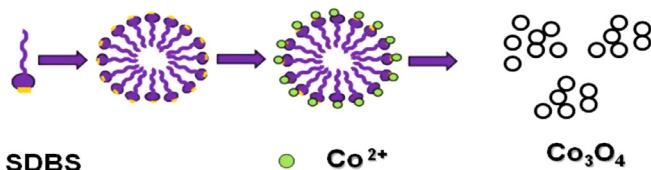
The stability evaluation for OER was performed by CV cycling between the electrode potential from 0.8 V to 1.5 V at 50 mV/s for 1000 cycles. Before and after the CV cycling, the LSV curves for the OER were measured, respectively.

3. Results and discussion

3.1. Catalyst characterizations

The synthesis of Co_3O_4 nanoparticles with the assistance of SDBS as the soft template is schematically illustrated in Scheme 1. It is worth noting that the saturated SDBS in deionized water will form micelles with sphere-like shape. The hydrophilic terminal will absorb the Co^{2+} ion directly and then the Co^{2+} ion will nucleate and grow along the chains of SDBS. That is, active Co_3O_4 monomers gradually grow into clusters. The porous structure can be formed after the removal of the SDBS after the heat-treatment. Moreover, different Co^{2+} was adsorbed onto different terminal, which can enhance the uniformity of the Co_3O_4 , which contributes to the decrease of the catalysts particle size. Thus, the catalysts cluster can be formed, comprising of many small particles. Moreover, the removal of SDBS can also improve the porosity of Co_3O_4 . Comparatively, without the assistance of SDBS, the particles favor aggregation during the synthesis process.

The crystalline structures of Co_3O_4 -S nanoparticles were investigated by X-ray diffraction (XRD) along with Co_3O_4 -T for comparison.



Scheme 1. Synthesis process of Co_3O_4 -S.

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