Template growth of ultrasmall Co$_3$O$_4$ nanoparticles: a high-efficiency electrocatalyst for alkaline oxygen evolution reaction

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Abstract. Co$_3$O$_4$, a representative spinel, has received widespread attention owing to its incomparable activity, low cost, and good stability, especially electrocatalytic performance for oxygen evolution reaction (OER). During the development of spinel synthesis, some emerging synthesis methods have been developed, and the transition from the high-temperature solid phase to the low-temperature liquid phase becomes a trend. Herein, we synthesized a class of novel small-sized Co$_3$O$_4$ nanoparticles using ZIF-8 polyhedrons as templates. Interestingly, the achieved Co$_3$O$_4$ nanoparticles possess smaller crystal sizes and good dispersibility, providing abundant active sites for OER reaction. When used as an OER electrocatalyst, the Co$_3$O$_4$-ZIF8 nanoparticles exhibit high efficiency with an overpotential of 270 mV at 1 mA cm$^{-2}$ and a small Tafel slope of 82.0 mV dec$^{-1}$. This study provides new insights into the preparation of Co$_3$O$_4$-based nanoparticles for applications in catalysis, energy storage, and sensors.

1. Introduction

Since the two industrial revolutions, while benefiting from the success of advanced industry, people are also deeply affected by the environmental pollution and energy exhaustion caused by fossil fuels and other energy sources. Therefore, new energy has become a hot topic of current and future research. Among them, hydrogen is considered as one of the most promising energy sources in the 21st century because of its environmental friendliness, non-pollution and high energy density [1, 2]. Electrocatalytic water splitting is currently a widely recognized way to obtain hydrogen [3-5]. But for now, the inert dynamics (high electric potential) of oxygen evolution reaction (OER) severely restricts the development of electrocatalytic water splitting from the theory to practical application [6-8]. Therefore, the research of high efficiency oxygen evolution catalysts is of great strategic significance.

In recent years, cobalt tetroxide (Co$_3$O$_4$), has been widely and deeply studied [9-11] due to its unique physical/chemical properties and potential applications in electrochemical energy conversion and storage, such as water splitting, lithium ion batteries and supercapacitors [12-14]. Furthermore, the high OER activity and low cost of Co$_3$O$_4$ make it a promising alternative to precious metals catalysts, such as RuO$_2$ and IrO$_2$. For these reasons, a large number of nano-sized Co$_3$O$_4$ catalysts have been designed and synthesized in the hope of improving their OER activity [15-18]. It is well known that controlling
the size of Co$_3$O$_4$ to the nanometer level can effectively increase its catalytic activity as OER electrocatalysts by increasing its exposed active sites.

Although lots of researches on nanosized Co$_3$O$_4$ crystals have been reported in recent years, most of them are prepared by electrodeposition, oil phase or solvothermal in small doses. In this work, the classical synthesis route was improved and pure Co$_3$O$_4$ nanoparticles was synthesized by the heat treatment of suitable ZIF-8 template. The OER activity of the small-sized Co$_3$O$_4$ nanoparticles with good dispersibility was studied. The results show that as-prepared Co$_3$O$_4$ nanoparticles can exhibit a small overpotential of 270 mV, a low Tafel slope of 82.0 mV dec$^{-1}$, and a remarkable stability, which is superior to the mostly reported Co-based oxide electrocatalysts.

2. Experimental Section

2.1. Synthesis of ZIF-8

0.8 g of Zn(NO$_3$)$_2$•6H$_2$O and 0.53 g of 2-methylimidazole were dissolved in 40 mL of methanol, respectively. Next, the two solutions were mixed and stirred for 20 min at room temperature. Then, the solution was injected into a Teflon lined reaction kettle and kept at 100 °C for 12 h. After that, the reactor was naturally cooled to room temperature. The product in the reactants was washed with anhydrous ethanol for three times. Centrifuge was used for separation after each washing. Finally, as-obtained product was dried at 60 °C under vacuum for 12 h.

2.2. Preparation of the mixture of ZnO and Co$_3$O$_4$ with ZIF-8 as the template

0.6 g of Co$_3$(NO$_3$)$_2$•6H$_2$O was dissolved in 10 mL of ethanol and stirred at room temperature. Then, 0.5 g of ZIF-8 prepared in (1) was added to the above solution. After stirring for another 2 h, the product was washed, and dried in a vacuum drying oven for 12 h. The product was then calcined at 600 °C for 5 h.

2.3. Preparation of Co$_3$O$_4$-ZIF8

The mixture of ZnO and Co$_3$O$_4$ prepared in (2) was dissolved in the buffer solution of NH$_4$Cl (5 M) - NH$_3$•H$_2$O (2.5 M). ZnO in the mixture reacted with the buffer solution to generate [Zn(NH$_3$)$_m$]$^{2+}$ and was removed. Finally, pure Co$_3$O$_4$ was obtained and labeled as Co$_3$O$_4$-ZIF8.

2.4. Preparation of Co$_3$O$_4$-ZIF67

0.45 g of Co$_3$(NO$_3$)$_2$•6H$_2$O was dissolved in 3 mL of anhydrous ethanol, and then 5.5 g of 2-methylimidazole was dissolved in 20 mL of anhydrous ethanol [19]. Next, the two solutions were mixed and stirred at room temperature for 6 h. After that, the ZIF-67 product was dried at 60 °C under vacuum for 12 h. The product was then calcined at 600 °C for 5 h. In the calcining process, ZIF-67 was decomposed to generate Co$_3$O$_4$, and the resulting product was labeled as Co$_3$O$_4$-ZIF67.

2.5. Material characterization

X-ray diffraction (XRD) was performed on Rigaku corporation UltimaV X-ray diffractometer using Cu Kα radiation (λ = 1.5406 Å). The morphologies of the Co$_3$O$_4$-ZIF8 and Co$_3$O$_4$-ZIF67 electrocatalysts were investigated using scanning electronic microscopy (SEM, Verios 460L) and high-resolution transmission electronic microscopy (TEM with FEG, Talos F200X).

2.6. Electrochemical measurements

2.6.1. Preparation of Co$_3$O$_4$-ZIF8 and Co$_3$O$_4$-ZIF67 electrodes. 5 mg of Co$_3$O$_4$-ZIF8 and Co$_3$O$_4$-ZIF67 were separately dispersed into 1 mL of mixture of aqueous Nafion (8% v/v) and ethanol (92% v/v), and ultra-sonicated for 30 min so as to obtain a homogeneous catalyst ink. All the as-prepared catalyst inks of Co$_3$O$_4$-ZIF8 and Co$_3$O$_4$-ZIF67 were then drop-cast onto the glass carbon electrode.
2.6.2. Test procedure. The OER performances of the catalyst were performed in a three-electrode system by employing a carbon rod as the counter electrode, Hg/HgO electrode as the reference electrode, and Co₃O₄-ZIF8 and Co₃O₄-ZIF67 as the working electrode, which were filled with O₂-saturated 1M KOH (pH = 14) electrolyte on a CHI760E electrochemical workstation (Shanghai Chenhua). The linear sweep voltammetry (LSV) measurements were conducted at 10 mV s⁻¹. Cyclic voltammetry (CV) tests were carried out between 0 V and 0.35 V at 10 mV s⁻¹. Electrochemical impedance spectra (EIS) were obtained at an open circuit potential with a frequency range from 100000 Hz to 0.01 Hz. All the potentials are calibrated with respect to a reversible hydrogen electrode (RHE, in 1 M KOH, \( E(\text{RHE}) = E(\text{Hg/HgO}) + 0.0591 \text{pH} + 0.098 \)).

3. Results and Discussion

![Figure 1](image1.png)

**Figure 1.** XRD pattern of Co₃O₄-ZIF8.

To investigate the crystalline phase and chemical constituents of Co₃O₄-ZIF8, XRD analysis was performed. As can be seen from the Figure 1, all the diffraction peaks are assigned to the cubic phase Co₃O₄ (JCPDS Card No. 42-1467) [20]. These characteristic diffraction peaks correspond to the (220), (311), (222), (400), (422), (511), (440) and (533) planes, respectively. Notably, except for the diffraction peaks of Co₃O₄, no other impurities peaks are found.

![Figure 2](image2.png)

**Figure 2.** TEM images (a, b) and HRTEM image (c) of Co₃O₄-ZIF8.

In order to explore the size and morphology of the Co₃O₄-ZIF8, TEM and HRTEM were carried out. Figures 2a and 2b show the TEM images of Co₃O₄-ZIF8, in which uniformly dispersed ellipsoidal nanoparticles with different sizes ranging from 5 nm to 30 nm could be seen, and no obvious agglomeration occurred. This is because the pore channels of the ZIF-8 crystal template and the gas
derived from thermal decomposition play a good role in inhibiting the agglomeration of the Co$_3$O$_4$ nanoparticles during the calcination process. As a result, the ZIF-8 polyhedron nanostructure acts as a template to synthesize small-sized Co$_3$O$_4$ nanoparticles with good dispersibility. Figure 2c shows the high-resolution TEM image of Co$_3$O$_4$-ZIF8. It can be seen that the lattice fringes of Co$_3$O$_4$-ZIF8 are clear and the lattice spacing is 0.24 nm, which is assigned to the (311) plane of the cubic phase Co$_3$O$_4$, corresponding to the XRD pattern in Figure 1.

Figure 3. The polarization curves and Tafel plots of OER on Co$_3$O$_4$-ZIF8 and Co$_3$O$_4$-ZIF67.

In order to investigate the OER performance of the synthesized catalyst, OER electrocatalytic activity was tested. Figure 3a shows the comparison of iR-corrected OER polarization curves of Co$_3$O$_4$-ZIF8 and the Co$_3$O$_4$-ZIF67 in 1 M KOH solution at 10 mV s$^{-1}$. The Co$_3$O$_4$-ZIF8 catalysts displayed a noticeable onset potential of 1.50 V vs. RHE, which is much lower than Co$_3$O$_4$-ZIF67 (1.60 V). Furthermore, to reach the current density of 10 mA cm$^{-2}$, the Co$_3$O$_4$-ZIF67 requires 1.71 V (vs. RHE), while the potential of the Co$_3$O$_4$-ZIF8 is only 1.63 V. Specifically, 400 and 480 mV overpotentials are required for the Co$_3$O$_4$-ZIF8 and Co$_3$O$_4$-ZIF67 electrodes to achieve the current density of 10 mA cm$^{-2}$.

The Tafel plots of the Co$_3$O$_4$-ZIF8 and Co$_3$O$_4$-ZIF67 catalysts are obtained by fitting the polarization curves to the Tafel equation to investigate the OER kinetics of the catalysts (Figure 3b). The Tafel slope of Co$_3$O$_4$-ZIF8 catalyst is 82.0 mV dec$^{-1}$, indicating that OER over Co$_3$O$_4$-ZIF8 follows the Volmer-Heyrovsky process [21]. The Tafel slope of Co$_3$O$_4$-ZIF67 has reached 148 mV/dec, which is much higher than Co$_3$O$_4$-ZIF8, indicating that the kinetic performance of the Co$_3$O$_4$-ZIF8 catalyst is better than that of the Co$_3$O$_4$-ZIF67 catalyst. The high OER activity of the Co$_3$O$_4$-ZIF8 can be attributed to the smaller crystal size and better dispersibility compared with Co$_3$O$_4$-ZIF67, which could provide abundant active sites to activate adsorbed water molecules, facilitating the OER process.

Figure 4. Stability of the Co$_3$O$_4$-ZIF8 after 1500 cycles.

Durability was another important indicator to evaluate an OER electrocatalyst. Figure 4 shows the stability curve of Co$_3$O$_4$-ZIF8 catalyst after 1500 cycles at 100 mV s$^{-1}$. After 1500 CV cycles, the polarization curve of the catalyst remained substantially unchanged. A little right shift was caused by a
small portion of the catalyst falling off the working electrode in the electrolyte solution during the cycle test. It is obvious that the oxygen evolution performance of Co$_3$O$_4$-ZIF8 catalyst is very stable. The low cost, high activity and good stability characteristics of Co$_3$O$_4$-ZIF8 catalyst suggest its promising application value.

4. Conclusion
In summary, we have synthesized a class of novel small-sized Co$_3$O$_4$ nanoparticles with good dispersibility using ZIF-8 polyhedrons as templates. The as-synthesized Co$_3$O$_4$ nanoparticles possess small-sized crystal sizes and high surface areas. These beneficial structures afford it excellent electrocatalytic performance towards the OER, exhibiting enhanced conductivity and electrocatalytic activity of oxygen evolution with the onset potential of 1.50 V and over potential of 270 mV in comparison with Co$_3$O$_4$-ZIF67. This simple strategy is expected to be extended to the synthesis of other defective metal oxides catalysts with potential applications in the fields of new energy production or environmental disinfection. The relative studies are in progress.

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