Co$_3$O$_4$ Hollow Polyhedrons as Bifunctional Electrocatalysts for Reduction and Evolution Reactions of Oxygen

Duo Dong, Yang Liu, and Jinghong Li*

1. Introduction

With the increasing demands of global energy and growing public concerns about the energy depletion of fossil fuels, it is very imperative to develop sustainable energy conversion and storage technologies. Although much attention has been made to develop efficient catalysts for ORR and OER, it is still highly desired to create new bifunctional catalysts. In this study, Co$_3$O$_4$ hollow polyhedrons are synthesized as efficient bifunctional electrocatalysts for ORR and OER by simple one-step annealing Co-centered metal–organic frameworks (ZIF-67). Due to the large specific surface areas and high porosity, the as-prepared Co$_3$O$_4$ hollow polyhedrons exhibit excellent electrocatalytic activities for ORR and OER in alkaline media. Co$_3$O$_4$ hollow polyhedrons show higher peak current density (0.61 mA cm$^{-2}$) with four-electron pathway than Co$_3$O$_4$ particles (0.39 mA cm$^{-2}$), better methanol tolerance and superior durability (82.6%) than commercial Pt/C electrocatalyst (58.6%) for ORR after 25 000 s. In addition, Co$_3$O$_4$ hollow polyhedrons also display excellent OER performances with smaller overpotential (536 mV) for 10 mA cm$^{-2}$ than Co$_3$O$_4$ particles (593 mV) and superior stability (86.5%) after 25 000 s. This facile one-step strategy based on metal–organic frameworks self-sacrificed templates can be used to develop the promising well-defined porous hollow metal oxides electrode materials for energy conversion and storage technologies.

D. Dong, Dr. Y. Liu, Prof. J. Li
Department of Chemistry
Beijing Key Laboratory for Analytical Methods and Instrumentation
Tsinghua University
Beijing 100084, China
E-mail: jhli@mail.tsinghua.edu.cn
DOI: 10.1002/ppsc.201600191

It is very important to exploit low-cost and efficient oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) electrocatalysts for the development of renewable-energy conversion and storage techniques. Although much attention has been made to develop efficient catalysts for ORR and OER, it is still highly desired to create new bifunctional catalysts. In this study, Co$_3$O$_4$ hollow polyhedrons are synthesized as efficient bifunctional electrocatalysts for ORR and OER by simple one-step annealing Co-centered metal–organic frameworks (ZIF-67). Due to the large specific surface areas and high porosity, the as-prepared Co$_3$O$_4$ hollow polyhedrons exhibit excellent electrocatalytic activities for ORR and OER in alkaline media. Co$_3$O$_4$ hollow polyhedrons show higher peak current density (0.61 mA cm$^{-2}$) with four-electron pathway than Co$_3$O$_4$ particles (0.39 mA cm$^{-2}$), better methanol tolerance and superior durability (82.6%) than commercial Pt/C electrocatalyst (58.6%) for ORR after 25 000 s. In addition, Co$_3$O$_4$ hollow polyhedrons also display excellent OER performances with smaller overpotential (536 mV) for 10 mA cm$^{-2}$ than Co$_3$O$_4$ particles (593 mV) and superior stability (86.5%) after 25 000 s. This facile one-step strategy based on metal–organic frameworks self-sacrificed templates can be used to develop the promising well-defined porous hollow metal oxides electrode materials for energy conversion and storage technologies.

It is very important to exploit low-cost and efficient oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) electrocatalysts for the development of renewable-energy conversion and storage techniques. Although much attention has been made to develop efficient catalysts for ORR and OER, it is still highly desired to create new bifunctional catalysts. In this study, Co$_3$O$_4$ hollow polyhedrons are synthesized as efficient bifunctional electrocatalysts for ORR and OER by simple one-step annealing Co-centered metal–organic frameworks (ZIF-67). Due to the large specific surface areas and high porosity, the as-prepared Co$_3$O$_4$ hollow polyhedrons exhibit excellent electrocatalytic activities for ORR and OER in alkaline media. Co$_3$O$_4$ hollow polyhedrons show higher peak current density (0.61 mA cm$^{-2}$) with four-electron pathway than Co$_3$O$_4$ particles (0.39 mA cm$^{-2}$), better methanol tolerance and superior durability (82.6%) than commercial Pt/C electrocatalyst (58.6%) for ORR after 25 000 s. In addition, Co$_3$O$_4$ hollow polyhedrons also display excellent OER performances with smaller overpotential (536 mV) for 10 mA cm$^{-2}$ than Co$_3$O$_4$ particles (593 mV) and superior stability (86.5%) after 25 000 s. This facile one-step strategy based on metal–organic frameworks self-sacrificed templates can be used to develop the promising well-defined porous hollow metal oxides electrode materials for energy conversion and storage technologies.

It is very important to exploit low-cost and efficient oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) electrocatalysts for the development of renewable-energy conversion and storage techniques. Although much attention has been made to develop efficient catalysts for ORR and OER, it is still highly desired to create new bifunctional catalysts. In this study, Co$_3$O$_4$ hollow polyhedrons are synthesized as efficient bifunctional electrocatalysts for ORR and OER by simple one-step annealing Co-centered metal–organic frameworks (ZIF-67). Due to the large specific surface areas and high porosity, the as-prepared Co$_3$O$_4$ hollow polyhedrons exhibit excellent electrocatalytic activities for ORR and OER in alkaline media. Co$_3$O$_4$ hollow polyhedrons show higher peak current density (0.61 mA cm$^{-2}$) with four-electron pathway than Co$_3$O$_4$ particles (0.39 mA cm$^{-2}$), better methanol tolerance and superior durability (82.6%) than commercial Pt/C electrocatalyst (58.6%) for ORR after 25 000 s. In addition, Co$_3$O$_4$ hollow polyhedrons also display excellent OER performances with smaller overpotential (536 mV) for 10 mA cm$^{-2}$ than Co$_3$O$_4$ particles (593 mV) and superior stability (86.5%) after 25 000 s. This facile one-step strategy based on metal–organic frameworks self-sacrificed templates can be used to develop the promising well-defined porous hollow metal oxides electrode materials for energy conversion and storage technologies.

Over recent years, a lot of materials have been explored as stable and efficient bifunctional electrocatalysts for ORR and OER, among which transition-metal oxides such as perovskite oxide,[11] and manganese oxide,[12] show excellent bifunctional electrocatalytic activities. In recent research, electroactive Co$_3$O$_4$ nanomaterials, respectively, exhibit high electrocatalytic activities for ORR,[13] and OER,[14,15] with the advantages of earth-abundant, low cost, and stability under alkaline conditions. To further increase the electrocatalytic activities, great efforts have been devoted to developing various morphologies of Co$_3$O$_4$ nanostructured electrocatalysts. Thus different structures of Co$_3$O$_4$ nanomaterials such as mesoporous nanoparticles,[16] ordered mesoporous sponges,[17] mesoporous nanowires,[18] nanoflakes,[19] and hollow nanosphere microspheres,[20] have been developed. Compared with above 0D, 1D, and 2D electrocatalysts, 3D porous structure can offer more active sites, specific surface areas, and multiple accessible channels for the interaction, which could increase the electrocatalytic activities for ORR and OER.[21] Therefore, it is necessary to develop 3D porous Co$_3$O$_4$ as efficient bifunctional electrocatalysts for ORR and OER.

Metal–organic frameworks (MOFs), an intriguing class of porous crystalline inorganic–organic hybrid materials, have attracted wide attentions because of fascinating advantages such as tunable pore sizes, large surface areas, high porosity, and multiple functionalities.[22–25] Built from the coordination of metal ions/clusters with electron-donating organic ligands, MOFs have been widely used in chemical sensors,[26] drug delivery,[27] gas storage/separation,[28] catalysis,[29] and luminescence.[30] Recently, MOFs have been utilized as novel self-sacrificed templates under the condition of thermal decomposition to prepare porous electrocatalysts with high electrocatalytic activities.[31] In this study, we prepared regular porous hollow polyhedral cobalt oxide (Co$_3$O$_4$ hollow polyhedrons) through a facile one-step pyrolysis of Co-based MOFs (ZIF-67). The Co$_3$O$_4$ hollow polyhedrons exhibited excellent bifunctional electrocatalytic
ORR and OER activities compared with particulate Co$_3$O$_4$ (Co$_3$O$_4$ particles) and higher methanol tolerance as well as durability than commercial Pt/C in alkaline media. The schematic diagram for illustrating the ORR and OER electrocatalytic principles of Co$_3$O$_4$ hollow polyhedrons is displayed in Figure 1. This kind of porous hollow polyhedral structures can not only provide larger specific surface areas and higher porosity to expose more electrocatalytic active sites, but also increase the electron conduction and diffusion with four-electron pathway to create multiple accessible channels to promote electrocatalytic activities. This facile method based on MOFs-templates may put forward a new idea for the development of many other well-defined porous hollow metal oxides electrode materials with low cost, environmental benignity, and high efficiency.

2. Results and Discussions

2.1. Material Preparation and Characterization

As displayed in Figure 2A, all the X-ray diffraction (XRD) diffraction peaks of synthesized ZIF-67 matched well with the patterns of simulated sample that published in the reported literature.[32] Co$_3$O$_4$ hollow polyhedrons were obtained by annealing ZIF-67 precursors in air. Figure 2B shows that all the XRD diffraction peaks of Co$_3$O$_4$ hollow polyhedrons were identical to corresponding patterns of Co$_3$O$_4$ (JCPDS 42–1467). No extra peak was revealed, demonstrating the high purity of the prepared hollow Co$_3$O$_4$. These results suggest that we successfully converted ZIF-67 into Co$_3$O$_4$ hollow polyhedrons.

Figure 1. Schematic diagram for illustrating the ORR and OER electrocatalytic principles of Co$_3$O$_4$ hollow polyhedrons.

Figure 2. XRD patterns of A) ZIF-67 and B) Co$_3$O$_4$ hollow polyhedrons.
The microstructure and morphology of ZIF-67 and Co$_3$O$_4$ hollow polyhedrons were characterized by scanning electronic microscopy (SEM). As shown in Figure 3A, ZIF-67 showed rhombic dodecahedral structures with smooth surface and the size was about 700 nm. After annealing ZIF-67 in air, the Co$_3$O$_4$ hollow polyhedrons became honeycomb-like morphology without microstructure damage (Figure 3B). The transmission electron microscopy (TEM) image confirms polyhedral structures with pores and rough surface. In addition, the obvious differences between centers and edges of the Co$_3$O$_4$ polyhedrons revealed its hollow interior structure (Figure 3C). As depicted in Figure 3D, high-resolution TEM (HRTEM) image presents the distance between the lattice fringes and the value of 0.248 nm was corresponded to the (311) plane of Co$_3$O$_4$. Figure 3E shows the selected-area electron diffraction (SAED) patterns of Co$_3$O$_4$ hollow polyhedrons with a series of well-defined rings, and these rings were assigned to the (111), (220), (311), (400), (511), and (440) planes of orthorhombic Co$_3$O$_4$, respectively. As displayed in Figure 3F, the compositional analysis measured through energy dispersive X-ray (EDX) spectroscopy presents uniform distributions of O and Co elements within the Co$_3$O$_4$ hollow polyhedrons, suggesting the formation of cobalt oxide.

The electronic states of Co$_3$O$_4$ hollow polyhedrons were further characterized by XPS spectroscopy. As depicted in Figure 4A, the XPS spectrum shows the prominent peaks of O and Co elements. Figure 4B displays that the Co 2p high-resolution XPS spectra contained two prominent peaks, which were belong to Co 2p$_{1/2}$ (780.5 eV) and Co 2p$_{3/2}$ (795.5 eV) peaks with spin–orbit splitting of 15.0 eV. The Co 2p deconvolution led to two spin–orbit doublets with Co$^{2+}$ (796.7 and 781.5 eV) and Co$^{3+}$ (795.2 eV and 780.2 eV). A weak satellite peak was detected in the spectra at 790.0 eV, which was an important Co$_3$O$_4$ phase characteristic. High-resolution XPS spectra contained three peaks with binding energies of 530.0, 530.5, and 531.5 eV being assigned to the lattice oxygen (O$_L$), oxygen vacancy (O$_V$), and chemisorbed oxygen (O$_C$), respectively.

For comparison, particulate Co$_3$O$_4$ (Co$_3$O$_4$ particles) was also applied. Figure S1A of the Supporting Information shows the XRD of Co$_3$O$_4$ particles, confirming its composition. The morphology of Co$_3$O$_4$ particles was displayed in Figure S1B of the Supporting Information, and it was clear that the sample was composed of lots of small particles with aggregation, which was significantly different from the prepared Co$_3$O$_4$ hollow polyhedrons. In addition, the specific surface areas and electrochemical impedance spectrum (EIS) of Co$_3$O$_4$ hollow polyhedrons and Co$_3$O$_4$ particles were also conducted. The surface areas and the porosity of Co$_3$O$_4$ hollow polyhedrons and Co$_3$O$_4$ particles were further analyzed by N$_2$ adsorption/desorption isotherms. As shown in Figure 5, Co$_3$O$_4$ hollow polyhedrons showed larger BET surface areas and smaller pore-size than Co$_3$O$_4$ particles. The BET surface area of Co$_3$O$_4$ hollow polyhedrons was calculated to be about 49.27 m$^2$ g$^{-1}$, while for Co$_3$O$_4$ particles, it was only about 18.62 m$^2$ g$^{-1}$. The average pore-sizes of Co$_3$O$_4$ hollow polyhedrons and Co$_3$O$_4$ particles were 28.53 and 41.67 nm, respectively. The higher specific surface areas and smaller pore-size may provide more electrocatalytic active sites. Moreover, the electrochemical impedance spectroscopies of Co$_3$O$_4$ hollow polyhedrons and Co$_3$O$_4$ particles to investigate the interfacial electrical properties were tested in 5 x 10$^{-3}$ M Fe(CN)$_6^{3-}$/4- containing 0.5 M KCl from 0.1 Hz to 100 kHz with 10 mV signal amplitude (Figure S2, Supporting Information). Inset in Figure S2 of the Supporting Information depicts the equivalent circuit, and the fitting charge transfer resistance ($R_q$) values of Co$_3$O$_4$ hollow polyhedrons and Co$_3$O$_4$ particles were 286.8 and 840.9 Ω, respectively. These results suggest that
Co₃O₄ hollow polyhedrons owned faster electron conduction and diffusion ability.

2.2. Electrocatalytic Performances of ORR and OER

To investigate the electrocatalytic ORR performances of Co₃O₄ hollow polyhedrons, cyclic voltammogram (CV) curves were measured in N₂- and O₂-saturated 0.1 m KOH solution with the catalyst loading of 0.170 mg cm⁻². As shown in Figure 6A, for Co₃O₄ hollow polyhedrons in N₂-saturated solution, no reduction peak was observed. In contrast, when Co₃O₄ hollow polyhedrons were tested in O₂-saturated solution, a distinct reduction peak appeared at 0.56 V with peak current density of 0.61 mA cm⁻², suggesting high electrocatalytic activities of Co₃O₄ hollow polyhedrons for ORR. For comparison, the ORR catalytic activities of ZIF-67 and Co₃O₄ particles were also measured (Figure 6B). It was seen that Co₃O₄ particles and ZIF-67, respectively, exhibited reduction peak at 0.52 and 0.56 V with peak current density of 0.39 and 0.27 mA cm⁻², which were both inferior than Co₃O₄ hollow polyhedrons. Also the ORR onset potential of Co₃O₄ hollow polyhedrons was earlier than Co₃O₄ particles. It is well known that the Co³⁺ cations at the Co₃O₄ surface could act as reduction sites with acceptor property by capturing electrons to Co₃O₄ and donor electronic character to oxygen in alkaline media.¹³ Larger specific surface areas of Co₃O₄ hollow polyhedrons than Co₃O₄ particles could generate more Co³⁺ cations at the surface to improve the ORR. These results imply that Co₃O₄ hollow polyhedrons could be

---

**Figure 4.** A) XPS survey of Co₃O₄ hollow polyhedrons. High-magnification XPS spectra in the B) Co 2p region and C) O 1s region of Co₃O₄ hollow polyhedrons.

**Figure 5.** A) N₂ adsorption/desorption isotherms and B) pore-size distributions of Co₃O₄ hollow polyhedrons and Co₃O₄ particles.
used as a promising electrocatalyst for ORR. Furthermore, the performance comparison of the Co$_3$O$_4$ hollow polyhedrons with other morphologies of Co$_3$O$_4$ electrocatalysts for ORR is shown in Table S1 of the Supporting Information.

Previous researches suggested that two parallel pathways (efficient direct four-electron process and indirect two-electron process) were proceeded in ORR.[34] To investigate the ORR kinetics of Co$_3$O$_4$ hollow polyhedrons, rotating disk electrode (RDE) voltammetry was performed in O$_2$-saturated 0.1 M KOH solution with various rotation rates from 225 to 1600 rpm. As shown in Figure 6C, with increasing the rotation rate, the current density enhanced gradually, indicating an increase of O$_2$ diffusion at the surface of electrode. In addition, inset in Figure 6C depicts good linearity of Koutecky–Levich (K–L) plots from 0.45 to 0.35 V, suggesting similar electron transfer number ($n$) and O$_2$ first-order reaction kinetics in the ORR.

Figure 6D shows the linear sweep voltammetry (LSV) curves of different catalysts with RDE in O$_2$-saturated 0.1 M KOH solution at 1600 rpm. Co$_3$O$_4$ hollow polyhedrons showed higher current density than Co$_3$O$_4$ particles and ZIF-67, which was consistent with the CV observations, indicating more active sites and faster electron transfer of the prepared Co$_3$O$_4$ hollow polyhedrons.

Moreover, according to K–L equations, the electron transfer number ($n$) can be calculated from the slope

\[
\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_i} = \frac{1}{Bo^{1/2}} + \frac{1}{J_k}
\]

where $J$ is the measured current density, $J_k$ is the diffusion limiting current density, $J_i$ is the kinetic limiting current density, $\omega$ ($\omega = 2\pi N$, $N$ is the rotation rate) is the rotation speed (rad s$^{-1}$), $n$ is the electron transfer number in ORR, $F$ is Faraday constant (96 485 C mol$^{-1}$), $C_0$ is the O$_2$ concentration (1.1 $\times$ 10$^{-6}$ mol cm$^{-3}$), $D_0$ is the O$_2$ diffusion coefficient (1.9 $\times$ 10$^{-5}$ cm$^2$ s$^{-1}$) in the KOH electrolyte, $v$ is the electrolyte kinematic viscosity (1.0 $\times$ 10$^{-2}$ cm$^2$ s$^{-1}$) in 0.1 M KOH, and $k$ is the electron transfer rate constant.[35] The electron transfer number ($n$) of Co$_3$O$_4$ hollow polyhedrons calculated by K–L equations was about 3.82 at 0.35 V, which revealed an efficient four-electron pathway of oxygen reduction. However, the transfer number was 3.26 for Co$_3$O$_4$ particles, indicating two-electron process and four-electron process dominated together in ORR (Figure S3A, Supporting Information). And the transfer number of ZIF-67 was 2.39, indicating two-electron process dominated in ORR (Figure S3B, Supporting Information).

As a new kind of ORR catalyst, methanol-tolerance and durability are very important. As depicted in Figure 7A, no apparent change was observed for Co$_3$O$_4$ hollow polyhedrons after adding 3 M methanol, suggesting high methanol-tolerance ability. For the commercial Pt/C, a deep reduction peak appeared at 0.77 V with peak current density of 1.78 mA cm$^{-2}$, but there was no obvious
reduction peak after adding 3 M methanol (Figure 7B). The durability was tested through chronoamperometric measurements at 0.55 V in O₂-saturated 0.1 M KOH solution at a rotation rate of 1600 rpm. Figure 7C shows that the commercial Pt/C maintained only 58.6% of the original activity after 25 000 s, whereas the value of Co₃O₄ hollow polyhedrons was 82.6%, indicating the synthesized 3D hollow polyhedral structures owned high durability. These results indicate that the ORR activity of Co₃O₄ hollow polyhedrons was lower than commercial Pt/C, but the Co₃O₄ hollow polyhedrons showed better methanol tolerance and superior durability than commercial Pt/C and could be used as a promising electrocatalyst in direct methanol fuel cells for a long time.

Besides the high ORR activities, Co₃O₄ hollow polyhedrons also performed superior electrocatalytic activities in OER. The OER performances were measured using linear sweep voltammetry (LSV) in 1 M KOH solution by RDE at 1600 rpm with the catalyst loading of 0.205 mg cm⁻². As revealed in Figure 8A, bare GCE showed negligible OER activities while ZIF-67 exhibited improved OER activities with onset overpotential of 546 mV and small current density. When Co₃O₄ particles were applied, the anode current density was further increased, indicating moderate OER activities of Co₃O₄ particles. It was surprising that Co₃O₄ hollow polyhedrons showed stronger OER activities with earlier onset overpotential (436 mV) and higher current density (overpotential of 536 mV to achieve 10 mA cm⁻²) than those of Co₃O₄ particles (onset overpotential of 466 mV and overpotential of 593 mV to achieve 10 mA cm⁻²). As a high performance OER standard, commercial RuO₂ showed earlier onset overpotential (292 mV) and overpotential (391 mV) to achieve 10 mA cm⁻², but with the potential increasing, the current densities of Co₃O₄ hollow polyhedrons and commercial RuO₂ got closer. Furthermore, the performance comparison of the Co₃O₄ hollow polyhedrons with other morphologies of Co₃O₄ electrocatalysts for OER is shown in Table S2 of the Supporting Information.

In addition, the OER kinetics of various electromaterials were studied by analyzing Tafel plots of Tafel equation \( \eta = a + b \log j \), of which \( b \) is Tafel slope and \( j \) is current density.\(^{[36]}\) As shown in Figure 8B, the Tafel slopes resulted from linear fitting of Tafel plots were 57, 61, 74, and 51 mV dec⁻¹ for Co₃O₄ hollow polyhedrons, Co₃O₄ particles, ZIF-67 and commercial RuO₂, respectively. The smallest Tafel slope suggested that it could provide a greatly improved OER rate to decrease the overpotential to achieve 10 mA cm⁻². At last, we tested the long-term durability of Co₃O₄ hollow polyhedrons at 536 mV overpotential in 1 M KOH at a rotation rate of 1600 rpm. Figure 8C depicts that Co₃O₄ hollow polyhedrons maintained 86.5% of the original activities after 25 000 s, indicating high stability. These results suggest that Co₃O₄ hollow polyhedrons could also be used as a promising electrocatalyst for OER in practical applications.

As we know, the electrochemical activities of catalyst could be seriously affected by the size of catalysts, so we also investigated the ORR and OER performances of Co₃O₄ hollow polyhedrons with different sizes. For comparison, 300 and 100 nm Co₃O₄ hollow polyhedrons were prepared by modulating the ratio of Co(NO₃)₂·6H₂O and 2-methylimidazole.
Figure S4A of the Supporting Information shows the XRD patterns of the synthesized 300 and 100 nm samples. All the XRD diffraction peaks of 300 nm and 100 nm samples were identical to Co$_3$O$_4$ (JCPDS 42–1467), indicating the formation of pure Co$_3$O$_4$. Figure S4 of the Supporting Information displays the SEM images of the prepared ZIF-67 and Co$_3$O$_4$ of 300 and 100 nm. It was clear that the 300 and 100 nm Co$_3$O$_4$ hollow polyhedrons owned similar morphology and structure with 700 nm Co$_3$O$_4$ hollow polyhedrons. Figure S5 of the Supporting Information compares the ORR performances of Co$_3$O$_4$ with different sizes. 700 nm Co$_3$O$_4$ hollow polyhedrons exhibited highest peak current density ($0.61 \text{ mA cm}^{-2}$) than those of 300 nm Co$_3$O$_4$ hollow polyhedrons ($0.52 \text{ mA cm}^{-2}$) and 100 nm Co$_3$O$_4$ hollow polyhedrons ($0.50 \text{ mA cm}^{-2}$) in O$_2$-saturated 0.1 m KOH solution. Additionally, the OER performances of Co$_3$O$_4$ with different sizes were also evaluated using LSV in 1 m KOH. As displayed in Figure S6 of the Supporting Information, 700 nm Co$_3$O$_4$ hollow polyhedrons showed smallest onset overpotential and highest current density ($436 \text{ mV onset overpotential and 536 mV overpotential to achieve 10 mA cm}^{-2}$) than those of 300 nm Co$_3$O$_4$ ($439 \text{ mV onset overpotential and 555 mV overpotential to achieve 10 mA cm}^{-2}$) and 100 nm Co$_3$O$_4$ ($441 \text{ mV onset overpotential and 569 mV overpotential to achieve 10 mA cm}^{-2}$). Moreover, the kinetics of Co$_3$O$_4$ with different sizes were also characterized by electrochemical impedance spectroscopy (EIS) in $5 \times 10^{-3}$ m Fe(CN)$_6^{3-/4-}$ containing 0.5 m KCl from 0.1 Hz to 100 kHz with 10 mV signal amplitude (Figure S7, Supporting Information). 700 nm Co$_3$O$_4$ hollow polyhedrons revealed the smallest charge transfer resistance, indicating fastest electron conduction ability. Therefore, we inferred that the highest ORR and OER activities of 700 nm Co$_3$O$_4$ hollow polyhedrons might result from superior electron transfer ability.

Based on the above results, we could discuss the origin of superior ORR and OER performances of Co$_3$O$_4$ hollow polyhedrons compared with Co$_3$O$_4$ particles. First, the polyhedral hollow morphology can provide larger specific surface areas and higher porosity, which may expose more electrocatalytic active sites. Second, faster electron conduction and diffusion of polyhedral hollow morphology with four-electron pathway can provide multiple accessible channels to promote the ORR and OER activities.

3. Conclusion

In this study, we report a facile one-step synthesis of porous hollow Co$_3$O$_4$ polyhedrons through annealing ZIF-67, which can be used as efficient bifunctional electrocatalysts for ORR and OER. Compared with Co$_3$O$_4$ particles, Co$_3$O$_4$ hollow polyhedrons not only exhibit excellent catalytic performances, but also show better long-time durability. This kind of porous hollow polyhedral structures can provide larger specific surface areas and higher porosity to expose more electrocatalytic active sites. Moreover, the polyhedral hollow morphology can increase the electron conduction and diffusion with four-electron pathway to create multiple
accessible channels to promote electrocatalytic activities. The raw materials used to prepare Co$_3$O$_4$ hollow polyhedrons are inexpensive and the one-step pyrolysis process is simple. Since the MOFs could be synthesized with various morphologies and compositions, this facile strategy based on MOFs-templates can be applied to prepare many other well-defined porous hollow metal oxides electrocatalysts used in energy technologies with promising electrochemical performances.

4. Experimental Section

**Materials:** 2-methylimidazole was purchased from Acros. Particulate Co$_3$O$_4$ was purchased from Sinopharm Chemical Reagent. Commercial 20% Pt/C catalyst was purchased from PEMEAS Fuel Cell Technologies. Nafion emulsion (5 wt%) was purchased from Alfa Aesar. The other chemicals were purchased from Beijing Chemical Company and used without further purification.

**Synthesis of ZIF-67 and Co$_3$O$_4$ Hollow Polyhedrons:** The schematic diagram of synthesis procedure is shown in Figure 1 and ZIF-67 was synthesized by a modified reported method.[37] Typically 0.996 g of Co(NO$_3$)$_2$·6H$_2$O and 1.312 g of 2-methylimidazole were separately dissolved in 100 mL methanol. The latter ligand solution was added into the former salt solution under vigorous stirring. The mixture was stirred for 12 min and then aged for 24 h at room temperature. After that, the purple precipitate was centrifuged, washed with methanol three times and vacuum dried at 80 °C for 12 h. To prepare Co$_3$O$_4$ hollow polyhedrons, the above-prepared ZIF-67 precursors were annealed at 300 °C for 2 h in air and then cooled down naturally to room temperature.

**Characterization:** The X-ray diffraction (XRD) patterns were recorded using Bruker D8-Advance with Cu Kα radiation (λ = 1.5418 Å). The scanning electron microscopy (SEM) images were obtained via Hitachi SU8010 scanning electron microscope. The transmission electron microscopy (TEM) images and EDX spectroscopy analysis were recorded by means of JEM 2010 high-resolution transmission electron microscope. The X-ray photoelectron spectroscopy (XPS) analysis was measured through PHI Quantera scanning X-ray microprobe. The surface area and pore-size of Brunauer–Emmett–Teller (BET) were measured through PHI Quantera scanning X-ray microprobe and the surface area and pore-size of Brunauer–Emmett–Teller (BET) were measured through PHI Quantera scanning X-ray microprobe. The surface area and pore-size of Brunauer–Emmett–Teller (BET) were measured through PHI Quantera scanning X-ray microprobe. The surface area and pore-size of Brunauer–Emmett–Teller (BET) were measured through PHI Quantera scanning X-ray microprobe.

**Preparation of the Electrodes:** The glassy carbon electrodes (GCE) were polished using 300 nm alumina slurry to obtain a mirror-like surface and washed with ethanol and distilled water in ultrasonic bath for 5 min following by drying with N$_2$ airflow. 2 mg of catalyst was dissolved in 1 mL Nafion solution (0.5 wt%,aq) under sonication for 2 h to form a homogeneous catalyst ink (2 mg mL$^{-1}$). Subsequently, 6 and 20 µL of the homogeneous catalyst inks were coated onto the pretreated GCE of 3 and 5 mm in diameter, respectively. Before measurements, the working electrodes were dried for 12 h at room temperature.

**Electrochemical Measurements:** Electrochemical measurements were performed on CHI 1030B electrochemical workstation. A conventional three-electrode electrochemical cell was assembled with a Pt wire counter electrode, an Ag/AgCl (saturated KCl) reference electrode and a catalyst modified GCE working electrode. All the experiments were carried out at room temperature and the electrolyte solutions (KOH) were saturated with O$_2$ or N$_2$ prior to each measurement. All potentials were converted to reversible hydrogen electrode (RHE) scale: E (RHE) = 0.197 + 0.059 pH + E (Ag/AgCl).[38]

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This work was financially supported by National Key Research and Development Program of China (No. 2016YFA0203010), National Basic Research Program of China (No. 2013CB94004), National Natural Science Foundation of China (No. 51572139), and Tsinghua University Initiative Scientific Research Program.

Received: July 16, 2016
Revised: August 18, 2016
Published online: October 14, 2016


