Hollow-Structured Carbon-Supported Nickel Cobaltite Nanoparticles as an Efficient Bifunctional Electrocatalyst for the Oxygen Reduction and Evolution Reactions

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Abstract: Exploring efficient electrocatalysts for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is essential for fuel cells and metal-air batteries. In this paper, we developed 3D-hollow structured NiCo₂O₄/C nanoparticles with interconnected pores as bifunctional electrocatalysts which are transformed from solid NiCo₂ alloy nanoparticles based on Kirkendall effect. The unique hollow structure of NiCo₂O₄ nanoparticles increase the active sites and improve the contact with electrolyte, resulting in excellent ORR and OER performance. In addition, the hollow structured NiCo₂O₄/C nanoparticles exhibit superior long-term stability for both ORR and OER to commercial Pt/C. The template-free and surfactant-free synthesis strategy could be used for low-cost and large-scale synthesis of hollow structured materials, facilitating screening of high efficiency catalysts for energy conversion.

Introduction

The depletion of fossil fuel sources and environment pollution appeal the development of clean and renewable energy. Extensive attention has been focused on metal-air batteries and fuel cells for their excellent energy density as well as environmental friendly merits.^[1] For instance, lithium-air battery possess high theoretical energy density of approximately 5200 W h kg⁻¹ and optimal practical energy densities of 1700 W h kg⁻¹, which outperforms the state-of-art lithium battery and nearly comparable to gasoline.^[2] It is really desirable to use these new devices to meet the requirement of the development of society. To make the new device rechargeable, highly efficient bifunctional catalysts for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are really desirable to lower the overpotential so that promote the charge and discharge abilities.^[3] The reversible interconversion of water to O₂ and O₂ to water reactions make it possible for a reversible green energy conversion and storage device to harness energy.^[4] However, one of the challenges is the sluggish kinetics of the ORR in the cathode and the OER process in the anode for lithium-air batteries,^[3,5] which are the key steps to govern the charge and discharge process and the quality for metal-air batteries. Platinum-based catalysts have been widely recognized as the best catalytic materials for both ORR and OER.^[6] Nevertheless, the large scale production of Pt-based catalysts are restricted for its price, scarcity and cycling stability.^[7] Moreover, platinum based materials are sensitive to methanol, carbon monoxide or other low molecular weight organics.^[8] In addition, large overpotential lowered the energy efficiency of metal-air battery and fuel cells.^[9] Therefore, it is of vital important to develop alternative cost-effective bifunctional materials for both excellent ORR and OER activity to lower the electrochemical reaction overpotential.^[10]

Recently, 3d-transition metal based materials (e.g., Co, Ni, Fe and Mn) have attracted much attention and recognized as promising alternative catalytic materials applied in energy storage and conversion devices^[11] because of their superior merits, such as low cost, high durability, and barely aggregation during runtime in oxidation state in contrast to platinum or palladium-based noble metal nanomaterials.

In particular, the excellent ORR and OER catalytic performance revealed that the 3d-transition metal based materials would be optimal materials for metal-air batteries and fuel cells.^[10e] Ni based catalysts have been investigated as excellent OER catalysts in recent years.^[12] Besides, Co based materials are mostly investigated as high performance ORR catalyst in alkaline media.^[13] It is reported that the mixed valence transition metal oxides could make up the solid-state redox couples, like A³⁺/A²⁺, responsible for their notable catalytic performance.^[14] In addition, by introducing hollow structure or porosity in the 3d-transition metal based materials, the surface area and active sites for the particles would be enlarged and further enhance the electrochemical performance in the application of metal-air batteries,^[15] fuel cells,^[16] lithium battery^[17] as well as supercapacitors.^[18] Traditional synthetic approaches for hollow structured nanoparticles involve templates or surfactants. The tedious shell deposit approach and template removal steps limited the scalable production of such materials.^[19] Therefore, it is of great importance to develop a template- and surfactant- free method to produce hollow structured materials with both high ORR and OER performance. Herein, we report the preparation of hollow structured NiCo₂O₄ nanoparticles with interconnected pores as bifunctional electrocatalysts for ORR and OER in alkaline media. The hollow

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structure was formed based on Kirkendall effect,^[20] with no surfactants or templates used during the whole synthetic process. Electrochemical results indicate that the hollow structured NiCo_2O_4 nanoparticles outperformed $\text{Co}_3\text{O}_4/\text{C}$, NiO/C and NiCo_2/C for the ORR, exhibiting a dominant 4-electron pathway. Moreover, the unique hollow structured NiCo_2O_4 nanoparticles exhibit superior OER performance and long-term stability in comparison to commercial Pt/C .

Results and Discussion

The crystal structure of hollow $\text{NiCo}_2\text{O}_4/\text{C}$ nanoparticles was characterized by XRD. As shown in Figure 1a, carbon supported NiCo_2 alloy was formed by reducing homogeneous mixture of NiCl_2 , CoCl_2 and Vulcan XC-72 precursor under flowing H_2 in a tube furnace at 350°C . The broad peak at around 25° is correspond to (002) peak of carbon support. The other three diffraction peaks at 44.5° , 51.8° , 76.4° can be well indexed as (111), (200), (220) lattice planes of NiCo_2 alloy and slightly shift to the lower angle in contrast to the enlarged (220) diffraction peak of Ni/C from the inset graph of Figure 1a. The shift of XRD peak indicated that cobalt atom entered the crystal lattice of nickel resulted in the lattice expansion of nickel. From the surface segregation energies principle, we can see cobalt atom served as the solute exhibit strong anti-segregation which would result in nickel segregation on the particle surface.^[21] The hollow structure could be obtained at a proper oxidation temperature based on Kirkendall effect, for which the diffusion rate of metal atoms to the surface is faster than that of oxygen diffuses to the bulk, leaving voids inside of the particles.^[22] The optimal oxidation temperature was chosen from TGA measurement (Figure S1a). It can be seen that the weight percentage gradually increase with temperature, which would be explained by the transformation of metal into metal oxides. When the temperature increased over 400°C , a sharp weight loss was observed because of the combustion of carbon support.

Figure 1. XRD patterns of (a) solid structure Ni/C , Co/C , NiCo_2/C nanoparticles and its subsequent oxidation products of (b) hollow structured NiO/C , $\text{Co}_3\text{O}_4/\text{C}$, $\text{NiCo}_2\text{O}_4/\text{C}$ nanoparticles.

In terms of the TGA curves, 300°C was chosen as the optimal temperature for oxidizing Ni/C , Co/C and NiCo_2/C , while lower or higher temperature would result in incomplete oxidation of the samples or severe mass loss of carbon support, respectively. The atomic percentage of Ni and Co in $\text{NiCo}_2\text{O}_4/\text{C}$ nanoparticles was measured by using X-Ray fluorescence (XRF) to be about 34.05% and 65.95%, which is approximately 1 : 2 (Figure S2), in consistent with the nominal ratio of Ni to Co. The successful transformation of metallic Ni, Co and NiCo_2 alloys to oxides was verified by XRD in Figure 1b. The diffraction peaks at 18.9° , 31.2° , 36.7° , 44.6° , 59.1° , 64.9° in the blue line attributed to (111), (220), (311), (400), (511) and (440) lattice planes, in consistent with the standard diffraction pattern of NiCo_2O_4 (JCPDS No. 02-4211). In addition, the XRD patterns of Ni/C , Co/C and their corresponding oxides were also seen in Figure 1. The weight percentage of bimetallic oxides and metal oxides is approximately 28 wt% from TGA measurement (Figure S1b).

Figure 2. (a-b) BF-STEM and DF-STEM overview of NiCo₂/C nanoparticles; (c-e) DF-STEM image of one NiCo₂ particle and the corresponding EELS elemental mapping of Co, Ni and overlay of Ni and Co.

The microstructure and chemical composition of bimetallic NiCo₂/C and NiCo₂O₄/C nanoparticles are characterized by transmission electron microscopy (TEM), bright field scanning transmission electron microscopy (BF-STEM) and dark field scanning transmission electron microscopy (DF-STEM) equipped with electron energy loss spectra (EELS). We can see from Figure 2a that solid structured NiCo₂ nanoparticles supported on Vulcan XC-72 are relatively uniform distributed with diameter ranging from 40 nm to 70 nm. Figure 2b shows the DF-STEM image of a NiCo₂ alloy particle which is smooth on the surface. Its corresponding EELS elemental distribution is shown in Figure 2(c-e). We can see that the Co and Ni atoms are uniformly distributed inside the solid particle but with Ni-rich shell on the surface of the particle which is fully in consistent with the surface segregation energy principle.^[21]

The NiCo₂ alloy was gradually oxidized in a stationary air at 300 °C. Based on the Kirkendall Effect, nickel and cobalt atoms inside of the particles slowly diffused to the surface, while oxygen diffused into the particles. Surface composition of the bimetallic alloy is very sensitive to the external conditions such as in O₂ atmosphere which may result in opposite element composition in comparison to the alloy in H₂ atmosphere.^[23] As the outward diffusion of metal atoms, hollow structure formed after oxidation of the alloy. Figure 3a shows the DF-STEM image of NiCo₂ alloy after oxidation. It can be clearly seen that the previous solid NiCo₂ alloy particles (Figure 2) transformed to hollow structured NiCo₂O₄ nanoparticles with hollow cavities ranging from 20 nm to 40 nm and particle size ranging from 40 to 70 nm. In the oxidation process, the inner metal atom for the NiCo₂ alloy would gradually move to the outer wall for the combination with oxygen. However, due to the different migration rate between Ni and Co atoms as well as the difference in crystal orientation, the location of hollow structure in a nanoparticle would make a difference. As shown in Figure S3a, we can clearly identify the hollow cavity from a nanoparticle which caused by the different contrast due to the extreme transmission intensity under high voltage vacuum condition. The hollow structure was located at different position with interconnected pores. Moreover, we can see interconnected pores more clearly for one NiCo₂O₄ particle from the tomographic reconstruction image in Figure S3b. Compared with Figure 2a, we can see that not only the crystal morphology changed, but also the crystal size decreased. The decreasing of crystal size could also be verified from the decreased intensity of diffraction peaks in the XRD patterns (Figure 1b). The inter-planar spacing between adjacent fringes in Figure 3b are measured to be 0.46 nm and 0.24 nm from high resolution transmission electron microscopy (HRTEM) image of an individual particle (inset of Figure 3b) corresponding to (111) and (311) planes, respectively. The lattice fringes in HRTEM image are consistent with the theoretical inter-planar spacing from the XRD patterns (Figure 2b). Figure 3c presents a DF-STEM image of a single NiCo₂O₄ nanoparticle, depending on the different contrast of outer wall and the interior for the particles, obvious hollow structure with a 20 nm cavity can be seen. Moreover, in contrast to the solid NiCo₂ particle, the original smooth surface was replaced by rough surface after a complete oxidation of NiCo₂ alloy. The EELS elemental distribution analysis in Figure 3(d-g) show a cobalt rich shell which is opposite to the solid NiCo₂ particle, probably attributed to the higher binding energy of Co-O than that of Ni-O,^[24] causing Co diffused faster than Ni to the particle surface. The formation of hollow structure could provide more active sites by increasing the surface area, facilitating the contact between oxygen and electrolyte. As shown from the nitrogen adsorption-desorption isotherms in Figure S4, the surface area increased from 145.2 m² g⁻¹ to 164.1 m² g⁻¹ after oxidation of NiCo₂ alloy particles.

Figure 3. (a) DF-STEM overview of hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ nanoparticles; (b) HRTEM image for a hollow structured NiCo_2O_4 particle; (c-g) DF-STEM image of a NiCo_2O_4 particle and the corresponding EELS elemental mapping of Co, Ni, O and overlay of Ni and Co.

The electrocatalytic activities of the materials for ORR were first evaluated by cyclic voltammetry (CV) measurement in N_2 - and O_2 -saturated 0.1 M KOH solution at a scan rate of 50 mV s^{-1} (Figure S5). The CVs comparison of the hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ and alloyed NiCo_2/C particles in N_2 -saturated KOH solution clearly show that the formation of hollow structure boosted the double-layer current, indicating the enlargement of surface area of materials, which agree with the BET measurement in Figure S4. Moreover, the hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ shows obvious oxygen reduction peak at around 0.70 V, while the peak is at around 0.67 V on NiCo_2/C electrode in O_2 -saturated solution. The oxygen reduction peak is about 30 mV positive, indicating an enhancement of ORR performance on hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ hybrid composite.

To gain further insight on the ORR electrocatalytic activity, ORR polarization curves were measured on different catalysts by using a rotating disk electrode (RDE) in O_2 -saturated 0.1 M KOH solution at a rotation rate of 1600 rpm and a scan rate of 5 mV s^{-1} . As shown in Figure 4a, the hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ nanoparticles exhibit the best electrocatalytic activity for ORR among these non-Pt electrocatalysts, with a half wave potential ($E_{1/2}$) of 0.71 V vs. RHE. Although the ORR activity is lower than that on commercial Pt/C ($E_{1/2}$ is 0.80 V), the cost of this kind of catalysts is much lower than Pt. Apparently, the lower half-wave potential (0.66 V) and limit current density (4.9 mA cm^{-2} , Figure R3) of NiCo_2/C indicated the necessity for the formation of hollow structure. It is noteworthy that the lower half wave potential and limit current density of directly oxidized $\text{NiCo}_2\text{O}_4/\text{C}$ (denoted as D- $\text{NiCo}_2\text{O}_4/\text{C}$) revealed great advantage for the novel two-step method. In order to investigate the influence of mixed valence for the catalytic performance, we compare the CV curves (Figure S6) of hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$, NiO/C and $\text{Co}_3\text{O}_4/\text{C}$ with same mass loading of metal on the electrode (Figure S1) at a potential range from 0.05 V – 1.4 V with a scanning rate of 50 mV s^{-1} in N_2 -saturated 0.1 M KOH solution. In comparison to the small redox peaks from region I for hollow structured $\text{Co}_3\text{O}_4/\text{C}$ and NiO/C , hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ exhibited obvious oxidation peaks at region II and two reduction peaks at regions III and IV. Thus, the enhanced electrocatalytic activity of $\text{NiCo}_2\text{O}_4/\text{C}$ (higher half-wave potential than hollow structured $\text{Co}_3\text{O}_4/\text{C}$ and NiO/C) is attributed to the changing of redox peaks by the substitute of Co to Ni.^[25] This result also indicated that O_2 is mostly easily reduced on NiCo_2O_4 catalyst.

The kinetics of the ORR on hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ nanoparticles was further explored on RDE electrode with different rotation rates (Figure 4b). Well defined diffusion limiting current can be clearly obtained. The inset in Figure 4b presents the corresponding Koutecky-Levich plots at various potentials obtained from the inverse of the current density $1/j$ vs. $\omega^{-1/2}$. Three paralleled straight line at three different potentials, indicated the first-order dependence of the kinetics for the ORR on hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ nanoparticles, similar to previous literatures.^[26] The electrons transfer numbers was calculated to be 3.89, 3.92, and 4.01 at potential of 0.55, 0.60, 0.65 V, respectively, suggesting a 4-electron ORR pathway for the hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ nanoparticles.

To better understand the mechanism of the ORR reaction pathway and hydrogen peroxide (HO_2^-) production, rotating ring-disk electrode (RRDE) measurement was performed on hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ nanoparticles. The electron transfer number (n) and HO_2^- production were calculated via equation (1) and (2) from RRDE voltammogram in the inset of Figure 4c, where the ring potential was set at 1.2 V. As for the two equations, j_D and j_R present the faradic disk current and the ring current, N equals to 0.37 represents the collection efficiency. At a rotation rate of 1600 rpm, the electron transfer number was calculated to be close to 4 at potential ranging from 0.1 V to 0.8 V, which is similar to commercial Pt/C (Figure S7). The HO_2^- yield was calculated to be less than 5 % below 0.8 V, suggesting the ORR process was dominant by a direct 4-electron pathway. The RRDE results on hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ are in consistent with the RDE results.

Figure 4. (a) ORR polarization curves on Vulcan XC-72, NiO/C , $\text{Co}_3\text{O}_4/\text{C}$, NiCo_2/C , D- $\text{NiCo}_2\text{O}_4/\text{C}$, $\text{NiCo}_2\text{O}_4/\text{C}$ and Pt/C in O_2 -saturated 0.1 M KOH solution at scan rate of 5 mV s^{-1} and rotation rate of 1600 rpm; (b) ORR polarization curves of $\text{NiCo}_2\text{O}_4/\text{C}$ in O_2 -saturated 0.1 M KOH solution at different rotation rates and the corresponding Koutecky-Levich plots of $\text{NiCo}_2\text{O}_4/\text{MWCNT}$ at potentials of 0.55 V, 0.6 V and 0.65 V (inset); (c) The electron-transfer number n , H_2O_2 yield and RRDE voltammograms (inset) on hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$; (d) i-t chronoamperometric stability measurement (at a constant potential of 0.6 V) on $\text{NiCo}_2\text{O}_4/\text{C}$ and Pt/C in O_2 -saturated 0.1 M KOH solution.

The stability performance for the electrode reaction is an integral part of considerations for the practical application of metal-air batteries and fuel cells. The durability of the hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ catalyst was measured using chronoamperometry method in comparison to commercial Pt/C, which was performed at a constant potential of 0.6 V for 10 h in O_2 -saturated 0.1 M KOH solution (Figure 4d). Remarkably, the corresponding current-time curve of hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ nanoparticles exhibits negligible current decay ($\sim 9\%$). In contrast, Pt/C suffers from a gradually decrease of current, with a current maintain of about 52% after 10 h. The durability results clearly indicate that the hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ nanoparticles exhibit superior long term stability for the ORR relative to Pt/C catalysts which is particularly desirable for metal-air batteries and fuel cells.

The oxygen evolution reaction (OER) catalytic performance of the hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ was investigated in N_2 -saturated 0.1 M KOH solution at a potential range from 0.9 V to 1.8 V with a rotation rate of 1600 rpm. As shown in Figure 5a, the hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ shows a high activity for OER, with the lowest onset potential of 1.25 V than other samples (1.35 V for NiO/C , 1.30 V for NiCo_2/C , 1.45 V for $\text{Co}_3\text{O}_4/\text{C}$ and 1.55 V for Pt/C). The OER current density on hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ is 25.6 mA cm^{-2} at 1.8 V,

which is outperformed $\text{Co}_3\text{O}_4/\text{C}$ ($\sim 15.8 \text{ mA cm}^{-2}$), NiCo_2/C ($\sim 18.4 \text{ mA cm}^{-2}$) and commercial Pt/C ($\sim 3.1 \text{ mA cm}^{-2}$), and close to NiO/C (26.1 mA cm^{-2}). The potential required at current density of 10 mA cm^{-2} ($E_{j=10 \text{ mA cm}^{-2}}$) represents a 10% efficient solar water-splitting device,^[13b, 27] which is commonly used to judge the OER activity. As for the hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$, $E_{j=10 \text{ mA cm}^{-2}}$ is about 1.67 V, which is much less positive than that of Pt/C (1.86 V, Figure 5b), indicating the hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ gives rise to a 10 mA cm^{-2} at small overpotential of 0.44 V. Despite that Pt exhibits higher ORR activity than hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ (Figure 4a, $E_{1/2}$ is 90 mV more positive), the OER activity is much worse ($E_{j=10 \text{ mA cm}^{-2}}$ is about 190 mV positive). It is worth noting that NiO/C exhibited a slightly better OER activity than $\text{NiCo}_2\text{O}_4/\text{C}$ ($E_{j=10 \text{ mA cm}^{-2}}$ is only about 4 mV negative), the ORR activity on NiO/C is much inferior to that of hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ (Figure 2a). The difference in potential between $E_{j=10 \text{ mA cm}^{-2}}$ and $E_{1/2}$ is usually used to evaluate the bifunctional catalytic activity of materials.^[13b] A small potential difference means better bifunctional catalytic activity. The value is about 960 mV for hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$, while it is 1060 mV for Pt/C .

The Tafel plots for OER on different electrodes were performed to further investigate the electrode kinetic. As shown in Figure 5c, the Tafel slope on hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ is $\sim 78.7 \text{ mV dec}^{-1}$, which is much lower than that of NiCo_2/C ($\sim 169.9 \text{ mV dec}^{-1}$), $\text{Co}_3\text{O}_4/\text{C}$ ($\sim 187.6 \text{ mV dec}^{-1}$) and Pt/C ($\sim 130.2 \text{ mV dec}^{-1}$), indicating a more favorable OER kinetic on hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$. The hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ exhibits not only superior bifunctional electrocatalytic activity, but also long-term stability. As shown in Figure 5d, the hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ exhibited excellent durability, with no current decay during 2000 continuous potential cycles. In comparison, Pt/C suffers from severe current decay and almost no catalytic activity remaining. Also, the chronopotentiometry test indicated that the hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ exhibited excellent potential stability at a constant current density of 10 mA cm^{-2} for 13000 seconds. While for Pt/C , there is a rapid potential increasing after only 700 s (Figure S8). The excellent electrocatalytic activity and durability suggest that hollow structured $\text{NiCo}_2\text{O}_4/\text{C}$ nanoparticles are promising bifunctional electrocatalyst for both ORR and OER.

Figure 5. (a) OER polarization curves on NiO/C , $\text{Co}_3\text{O}_4/\text{C}$, NiCo_2/C , $\text{NiCo}_2\text{O}_4/\text{C}$ and Pt/C measured in N_2 -saturated 0.1 M KOH solution at a rotation rate of 1600 rpm; (b) Potential comparison on different electrodes at 10 mA cm^{-2} from the polarization curves in (a); (c) Tafel plots of NiO/C , $\text{Co}_3\text{O}_4/\text{C}$, NiCo_2/C , $\text{NiCo}_2\text{O}_4/\text{C}$ and Pt/C recorded in N_2 -saturated 0.1 M KOH solution; (d) OER polarization curves of $\text{NiCo}_2\text{O}_4/\text{C}$ and Pt/C before and after 2000 cycles in N_2 -saturated solution.

Conclusions

In conclusion, the carbon supported hollow structured NiCo₂O₄ nanoparticles have been successfully prepared via a facile two-step method. The preparation procedure is simple, template- and surfactant- free, which is suitable for scalable production. The hollow structured hybrid showed much better electrocatalytic activity for both ORR and OER in comparison to single-metal oxides. Moreover, the NiCo₂O₄/C exhibits excellent durability for ORR and OER relative to Pt in alkaline solution. The reported synthesis provides a simple and cost-effective method for preparing hollow structured bimetallic oxide nanoparticles, offering a general approach for a promising new class of non-precious metal catalysts for metal-air batteries.

Experimental Section

Sample preparation. A “one-pot, two-step” strategy was developed to synthesize hollow structured NiCo₂O₄ nanoparticles supported on carbon^[16b,28]. NiCo₂ alloy nanoparticles were first synthesized via an impregnation-reduction method, and then oxidized in air to form hollow structured oxides based on Kirkendall effect^[22]. In detail, 108 mg CoCl₂•6H₂O, 54 mg of NiCl₂•6H₂O and 160 mg of Vulcan XC-72 were added into a 25 mL of baker. Then, 10 mL of purified water was poured into the baker followed by exchanging magnetic stirring and ultrasonic dispersion at 60 °C until the solution was evaporated to form thick slurry. The composite was then placed in a vacuum drying oven at 40 °C overnight and ensure sufficient drying. After the process of milling in agate mortar, the resulting powder was annealed in 350 °C for 3 h under H₂ atmosphere. The pre-prepared samples were then calcined in air at a heating rate of 1 °C min⁻¹ from room temperature to 300 °C and maintain for 10 h to obtain the final product. In comparison, Co₃O₄/C and NiO/C nanoparticles were synthesized under the same condition with a metal loading of 20 wt%.

The directly oxidized NiCo₂O₄/C (denoted as D- NiCo₂O₄/C) was obtained by directly oxidation of the mixed NiCl₂, CoCl₂ and Vulcan XC-72 precursor.

Physical characterization. Powder X-ray diffraction (XRD) was performed by using an X'Pert PRO diffractometer, and diffraction patterns were collected at a scanning rate of 4 °/min. Thermal gravimetric analysis (TGA) was conducted on TA-Q500 Instrument at a heating rate of 5 °C/min. X-Ray Fluorescence (XRF) was collected on EAGLE III, EDAX Inc. STEM tomographic images were obtained using 200 and 300 keV field-emission S/TEMs. Electron Energy Loss Spectroscopy (EELS) data were acquired using a Gatan Tridiem spectrometer.

Electrochemical measurements. All the electrochemical measurements were performed at room temperature (298 K) by using rotating disc electrode (RDE) and rotating ring-disc electrode (RRDE) with 5 mm-diameter glassy carbon substrate as working electrode. Carbon paper was used as counter electrode to eliminate the contamination from conventional Pt electrode, and reverse hydrogen electrode (RHE, $E^0 = -0.768$ V vs. SHE) was served as reference electrode in 0.1 M KOH solution. 5 mg of samples was dispersed in 1 mL isopropanol/Nafion hybrid solutions and ultrasonic dispersed to form homogeneous ink. 7.8 uL of ink (9.9 uL for RRDE) was dropped onto the glassy carbon substrate, and dried naturally. The loading quantity of commercial Pt/C is about 15 ug cm⁻². The RDE and RRDE performance of the samples are operated in O₂-saturated 0.1 M KOH solution at a sweep rate of 5 mV s⁻¹.

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