**Co₃O₄ nanoparticles embedded in nitrogen-doped porous carbon dodecahedrons
with enhanced electrochemical properties for lithium storage and water splitting**

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Abstract

A novel Co₃O₄/N-doped porous carbon hybrid with dodecahedrons structure was synthesized by a facile, two-step, thermal transformation of a cobalt-based zeolitic imidazolate framework. Well-dispersed Co₃O₄ nanoparticles were embedded in nitrogen-doped porous carbon networks, forming a unique nanopolyhedron. When tested as anode material for lithium-ion batteries, the hybrid exhibited superior electrochemical performance, including excellent rate capability of 560 mAh g⁻¹ at 10 A g⁻¹ which is close to 46% of the rate capacity at 100 mA g⁻¹, outstanding cycling stability with 91.7% capacity retention of the second cycle after 110 cycles, and considerably large discharge capacity of 1,730 mAh g⁻¹ at 100 mA g⁻¹. Moreover, the

hybrid also showed enhanced electrocatalytic activity for electrochemical oxygen evolution from water splitting.

Keywords: Co_3O_4 ; N-doped carbon dodecahedrons; Porous structure; Lithium-ion batteries; Water splitting

Introduction

The design and develop of economically feasible, highly active materials is at the heart of key energy conversion and storage technologies including water splitting and lithium-ion batteries (LIBs) [1-3]. Transition metal oxides are promising materials for LIBs and oxygen evolution reaction (OER) from water splitting processes because of their low cost and environmental friendliness [4, 5]. Among them, Co_3O_4 has been considered as one of the most promising candidates for both LIBs and OER [6, 7], due to its prominent advantages arising from high theoretical capacity (890 mAh g^{-1}) [8], low cost, environmental benignity, high corrosion stability, and excellent catalytic property. However, the practical application of Co_3O_4 is hindered by its large volume expansion/contraction, severe particle aggregation, and low electronic conductivity [9, 10]. To overcome these obstacles, one of the promising strategies is to construct hybrids consisting of Co_3O_4 and nanocarbons, particularly N-doped nanocarbons (such as N-doped carbon nanotubes [11], N-doped carbon foam [12], and N-doped graphene [6]). Notably, N-doped nanocarbons not only can act as a buffer layer to restrict volume expansion and aggregation of nanoparticles, but also serve as

complementary active sites for the OER and enhance the electronic conductivity of Co_3O_4 , thereby enhancing the overall electrochemical performance of electrodes [13, 14]. Even though many methods have been developed to synthesize various Co_3O_4 -based composites [15-19], the rational design and facile synthesis of Co_3O_4 nanoparticles well confined in the N-doped porous carbon networks with dodecahedrons architectures by an in-situ hybridization strategy, which can provide much more intimate interfacial contact than the approaches of ex-situ hybridization, still remains a big challenge.

Recently, zeolitic imidazolate frameworks (ZIFs) have attracted a considerable attention because of its fascinating properties and functions with modularly tunable structures assembled from transition-metal clusters as nodes and organic ligands as struts [20]. Inspired by their diverse configurations, ZIFs have been demonstrated as useful precursors/templates for the synthesis of metal oxides with controlled morphologies or porous carbon nanostructures via thermal decomposition under controlled atmospheres [21-23]. Nevertheless, the research on the synthesis of hybrid materials with homogeneously encapsulated metal oxides nanoparticles into N-doped carbon networks derived from ZIFs is still in its infancy. Only a few illustrations, including Co_3O_4 @N-doped carbon (derived from metal-organic frameworks (MOFs)) [24] and N-doped graphene/graphene-tube nanocomposite (derived from MOFs) [25], have been reported. Combining metal oxides nanoparticles with N-doped carbon networks to form a hybrid would integrate the advantages of its individual

components that can demonstrate a strong synergistic effect, thus enhancing the intrinsic properties of each component [26, 27]. Therefore, further improvement of this type of hybrid is highly desirable. Moreover, to the best of our knowledge, there has been no report on using ZIFs as the precursor/template to prepare metal oxide nanoparticles well confined in the N-doped porous carbon networks with dodecahedrons structure as bifunctional hybrid for both LIBs and OER. The use of a bifunctional hybrid not only can simplify the system, but also reduce the manufacturing cost and thus the cost of the resulting energy utilization.

Herein, we report a facile strategy for the fabrication of Co_3O_4 nanoparticles finely embedded in N-doped porous carbon networks ($\text{Co}_3\text{O}_4/\text{N-PC}$) with dodecahedrons structure by thermal decomposition of ZIF-67, as a bifunctional hybrid for both LIBs and OER. The ZIF-67 are chosen as precursor based on its advantages of abundant Co–N moieties and unique dodecahedral morphology [28-31]. Benefiting from a unique nanostructure, the resulting hybrid of $\text{Co}_3\text{O}_4/\text{N-PC}$ exhibits excellent electrochemical lithium-storage performance when used as the anode material in LIBs. Significantly, the obtained rate capability of the hybrid is almost the best rate capability among all the Co_3O_4 -based anode materials up to now. Moreover, beyond applications in LIBs, the hybrid also exhibits excellent OER catalytic activity comparable with that of commercial Ir/C catalyst.

Experimental section

Synthesis of $\text{Co}_3\text{O}_4/\text{N-PC}$: Firstly, ZIF-67 precursors were prepared according to a previous report [32]. Typically, 1.25 g of cobalt nitrate hexahydrate and 1.64 g of 2-methylimidazole were each dissolved in 125 mL methanol. The latter clear solution was added into the former pink solution with magnetic stirring. Stirring was stopped after combining the component solutions. The reaction was allowed to proceed at room temperature for 24 h, and the obtained purple product was collected through centrifugation and washed three times with methanol before being dried at 60 °C in air overnight for further use. Then, the prepared ZIF-67 product was transferred to a furnace and pyrolyzed under Ar atmosphere for 3 h at 900 °C with a rate of 2 °C min⁻¹, forming a Co/N/C composite (Figure S1). The resulting product was dispersed in 2 M H_2SO_4 solution and stirred for 12 h to partially remove metallic cobalt. Finally, the as-collected black product was loaded in a ceramic crucible, which was heated to 350 °C with a heating rate of 5 °C·min⁻¹ and maintained at 350 °C for 2 h under flowing Air to finally obtain the $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid.

Characterization: The morphology and composition of the $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid were characterized using a Hitachi H 9000 NAR transmission electron microscope (TEM) and a Hitachi S-4800 field emission scanning electron microscope (FESEM) equipped with an energy-dispersive X-ray spectroscopy analyzer. Powder X-ray diffraction (XRD) data was collected using a Scintag XDS 2000 X-ray powder diffractometer operating at 40 kV, 40 mA for Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Raman spectra were taken using a Raman spectrometer with a 633 nm laser excitation (Renishaw 1000B).

X-ray photoelectron spectroscopy (XPS) was performed using HP 5950A with Mg K α as the source and the C 1s peak at 284.6 eV as an internal standard. Thermogravimetric analysis (TGA) was carried out using a TA SDT 2960 thermoanalyzer with a heating rate of 5 °C min⁻¹ in air atmosphere. Nitrogen adsorption-desorption isotherm measurements were performed on a Micromeritics ASAP 2020 to study specific surface area. Before analysis, all samples were pretreated by degassing at 200 °C for 8 h to remove any adsorbed species.

Electrochemical Test:

(1) LIBs test

To evaluate the electrochemical performance of Co₃O₄/N-PC hybrid, CR2032-type coin cells were assembled in an argon-filled glove box with moisture and oxygen concentrations below 1.0 ppm. The working electrodes consisted of 80 wt.% of active material, 10 wt.% of Super P conductive carbon black, and 10 wt.% carboxymethyl cellulose (CMC). 1.0 M LiPF₆ in ethylene carbonate/ethyl methyl carbonate (40: 60, v/v) was used as electrolyte and lithium discs as the counter electrode and reference electrode. The charge-discharge tests were performed on a LAND CT2001A (Land, China) battery tester within the voltage range of 0.05-3.0 V. Cyclic voltammetry (CV) at a scanning rate of 0.1 mV s⁻¹ within the same voltage range and AC impedance over the frequency range from 100 mHz to 100 KHz with an amplitude of 5 mV was measured on a VersaSTAT 3F (Princeton Applied Research).

(2) OER test

Electrochemical measurements were performed in a standard three-electrode glass cell on a CH Instruments 760D electrochemical workstation using a glassy carbon electrode with various catalysts as the working electrode, a Pt wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. 0.1 M KOH was used as electrolyte. For the fabrication of the working electrode, 2.5 mg as-synthesized catalyst was mixed with 50 μL Nafion solution (5.0 % Nafion in ethanol) and 450 μL deionized water. The mixture was sonicated and 5.0 μL suspension was pipetted out and dropped onto a glassy carbon electrode with a diameter of 3 mm and then fully dried. All data were collected under O_2 saturation to ensure the $\text{O}_2/\text{H}_2\text{O}$ equilibrium at 1.23 V vs. RHE. Linear sweep voltammetry was carried out from 0.1 to 1.1 V (vs. Ag/AgCl) at 5 mV s^{-1} for the polarization curves and Tafel plots. The catalyst was cycled 50 times by CV until a stable CV curve was obtained before testing. The electrode potential reported in this work is relative to the reversible hydrogen electrode (RHE) potential, which was converted from the Ag/AgCl electrode using: $E_{\text{RHE}} = E_{(\text{Ag}/\text{AgCl})} + 0.9646 \text{ V}$ [33].

Results and discussion

Figure 1a illustrates the preparation procedure for the $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid. Firstly, highly uniform ZIF-67 nanoparticles with rhombic dodecahedral morphology were synthesized by a room-temperature precipitation method based on previous reports [32]. Then, conversion of ZIF-67 into $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid was performed by two-step

thermal treatments in a Ar and Air atmosphere, respectively. A detailed explanation of the procedures is given in the Experimental Section. Figure 1b shows the X-ray diffraction (XRD) pattern of the as-prepared Co₃O₄/N-PC hybrid. Two characteristic diffraction peaks at 25.85 and 42.53° are attributed to the graphite (002) and (100) planes of the graphitic carbon, while the other peaks can be readily indexed to cubic Co₃O₄ structure (JCPDS No. 42-1467), thus demonstrating that the hybrid consist of Co₃O₄ and graphitic carbon. This is supported by the Raman spectrum of the Co₃O₄/N-PC (Figure S2). The peaks at 186, 465, and 672 cm⁻¹ correspond to the F_{2g}, E_g, and A_{1g} modes of crystalline Co₃O₄, respectively [34-36]. Two broad peaks at 1,323 and 1,574 cm⁻¹ are the typical D and G bands of carbon materials [37]. The relative low intensity and the shift toward low frequency compared to those peaks of commercial Co₃O₄ reveal the well-dispersed nature of these small Co₃O₄ nanoparticles and their strong interactions with the N-PC [38-40]. Such strong synergistic effects would greatly promote the charge transfer between the Co₃O₄ and N-PC. The N-doping is ascertained by XPS survey spectrum, which shows five characteristic peaks located at ca. 285, 400, 530, 781, and 796 eV, corresponding to the C 1s, N 1s, O 1s, Co 2p_{3/2}, and Co 2p_{1/2}, respectively (Figure S3) [41]. The complex N 1s spectrum could be further deconvoluted into four peaks with binding energy values of 398.8, 400.3, 401.7, and 403.2 eV that correspond to pyridinic N, pyrrolic N, graphitic N, and oxidized N, respectively (Figure S3) [42]. The elemental content of N species in the Co₃O₄/N-PC hybrid is about 2.7 at.%. It is believed that

N-doping can enhance the electric conductivity of carbon-based materials and thus improve the electrochemical performance [43, 44].

The morphology of the as-prepared $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid was characterized by transmission electron microscopy (TEM). After annealing, well-defined porous $\text{Co}_3\text{O}_4/\text{N-PC}$ polyhedron hybrid are generated (Figure 1c), which consists of considerable Co_3O_4 nanoparticles and N-PC polyhedron. The porous structure (Figure S4) can be attributed to the graphitization of amorphous carbon catalyzed by Co metal [45]. The enlarged TEM image shows that most of Co_3O_4 nanoparticles with size of 15-30 nm were embedded within the N-PC networks, in which each nanoparticle was well dispersed without any aggregations (Figure 1d). A high-resolution TEM (HRTEM) image indicates that the observed lattice fringes spacing of 0.34 nm match well with the (002) planes of graphite (Figure 1e). The corresponding selected area electronic diffraction (SAED) investigations further verify the dark core being Co_3O_4 nanoparticles. Moreover, a close interfacial contact between Co_3O_4 nanoparticles and N-PC dodecahedrons was formed in the hybrid, which is beneficial for facilitating the fast charge transport and improving the overall electrochemical performance [46].

A typical field-emission scanning electron microscopy (FESEM) image of the $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid is shown in Figure 1f, suggesting that they consist of uniform polyhedral morphology. These polyhedra inherited well the rhombic dodecahedral shape of the ZIF-67 precursor except that the surface of polyhedra hybrid becomes more roughly (Figure S5 and Figure 1f). Additionally, it is clearly seen that the Co_3O_4

nanoparticles was well encapsulated in the N-PC dodecahedrons, which is consistent with TEM observations. The corresponding elemental mapping analysis of the $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid suggests the well-defined spatial distribution of all elements C, N, O, and Co in the hybrid. The Co_3O_4 content of $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid is estimated to be about 48.9% from thermogravimetric analysis (TGA, Figure S6). The amount of Co_3O_4 is comparable with other reported $\text{Co}_3\text{O}_4/\text{C}$ composites [8, 47, 48]. The nitrogen adsorption–desorption isotherm curves of the $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid showed a typical type IV with a H3 hysteresis loop at relative pressures P/P_0 of 0.4 to 1.0 (Figure S7), suggesting the presence of mesopores in the hybrid [49]. The Brunauer–Emmett–Teller (BET) surface area and average pore size of $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid were calculated to be $97 \text{ m}^2 \text{ g}^{-1}$ and 36 nm. Such a mesoporous architecture of the hybrid can offer the desirable combination of a highly accessible surface area and an efficient transport path, resulting in an improved electrochemical performance [50, 51].

The cyclic voltammetry (CV) curves of $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid in the potential window of 0.01 V–3.0 V at a scanning rate of 0.1 mV s^{-1} depicts an irreversible reduction peak at 0.69 V vs. Li/Li^+ in the first discharge process (Figure 2a). On the subsequent cathodic scans, one prominent peak is observed at 1.11 V accompanying with a slight peak at 2.16 V, which are attributed to the multistep reduction reactions of Co_3O_4 with Li^+ . While, the anodic sweeps show an oxidation peak at about 2.12 V corresponding to the formation of cobalt oxide [52]. Moreover, the CV profiles of hybrid is almost

identical to the Co_3O_4 nanoparticles (Figure S8), implying that the capacity in hybrid is dominantly contributed by Co_3O_4 in the hybrid (Figure 2c). Figure 2b shows the discharge/charge profiles of $\text{Co}_3\text{O}_4/\text{N-PC}$ at a current density of 100 mA g^{-1} in the 1st, 2nd, 10th, 20th, 50th, 70th, and 100th cycles. The first discharge curve depicts a long voltage plateau at 1.0 V followed by a sloping region down to the cutoff voltage of 0.01 V, which is consistent with previous reports [10, 52]. However, no discriminable plateau for C is observed, which is in well agreement with the CV observations. The hybrid exhibits an initial discharge/charge capacities of 1,730 and 1,321 mAh g^{-1} in the first cycle, corresponding to a Coulombic efficiency of 76.4% (Figure 2b-d). After 100 cycles, a charge capacity of 892 mAh g^{-1} is retained with a Coulombic efficiency close to 100% (Figure 2b-d). In contrast, the Co_3O_4 anode delivers a slightly higher discharge capacity (1,867 mAh g^{-1}) but suffers severe irreversible capacity loss, with a Coulombic efficiency of 51.3% in the first cycle (Figure 2d). Upon further charge/discharge, the Co_3O_4 anode demonstrates fast capacity fading, showing a discharge capacity retention only 9% of the initial cycle (180 mAh g^{-1}) after 50 cycles (Figure 2c). A controlled experiment using N-PC as active material reveals much lower specific capacity (Figure 2c), which is consistent with aforementioned CV observations and cycling tests. Notably, the $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid, with a Co_3O_4 concentration of 48.9%, delivered comparable capacity with pure Co_3O_4 but much stable cycling performance. The dramatically improved electrochemical performance of $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid in terms of initial cycle Coulombic efficiency and cyclability is

presumably due to its unique structural design which utilizes combinative merits of well dispersed Co_3O_4 nanoparticles and the high conductive N-doped porous carbon matrix, which not only enhances the electric and ionic conductivity but also be able to accommodate the volume expansion/contraction during cycling tests. Meanwhile, such superior performance may be attributed to the small nanoparticles of Co_3O_4 and high conductive porous carbon network structure which enables the full utilization of Co_3O_4 nanoparticles.

Moreover, the hybrid shows proficient cyclic stability at various current densities ranging from 50 mA g^{-1} to 10 A g^{-1} over 110 cycles (Figure 2e). The highest discharge capacity of $2,059 \text{ mAh g}^{-1}$ is achieved at the current density of 50 mA g^{-1} . When the current densities gradually increase, the $\text{Co}_3\text{O}_4/\text{N-PC}$ exhibits reversible capacities of $1,026 \text{ mAh g}^{-1}$ for the 60th cycle at 1 A g^{-1} , 947 mAh g^{-1} for the 70th cycle at 2 A g^{-1} , 839 mAh g^{-1} for the 80th cycle at 5 A g^{-1} , 627 mAh g^{-1} for the 90th cycle at 9 A g^{-1} , and 560 mAh g^{-1} for the 100th cycle at 10 A g^{-1} , corresponding to 84.3%, 77.8%, 68.9%, 51.4%, and 45.9% of the charge capacity for the 2nd cycle at 100 mA g^{-1} , respectively. When the current density changes back to 100 mA g^{-1} at 101th cycle, it reveals a charge capacity of $1,117 \text{ mAh g}^{-1}$, close to 91.7% of the 2nd cycle. Moreover, no obvious morphology change is observed after 100 cycles (Figure 3c), which demonstrates that a robust porous N-PC polyhedron can effectively accommodate the large volume change of Co_3O_4 during lithiation/delithiation. To the best of our knowledge, this is the highest rate capacity of Co_3O_4 -based anode

materials (Table S1). In contrast, pure Co_3O_4 suffers significant capacity loss with increased current densities, showing a charge capacity of 50 mAh g^{-1} at 70th cycle (Figure S9).

Additionally, the electrocatalytic activity of as-prepared $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid for OER is also evaluated (Figure 4a). Typically, the anodic current of $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid simultaneously increased as the potential became more positive, which was commonly observed for OER catalysts in alkaline media [6]. The $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid demonstrates a smaller onset potential of 1.52 V than that of Co_3O_4 (1.56 V) and N-PC (1.65 V), respectively; the onset potential of hybrid is only marginally higher than that of commercial Ir/C catalyst (1.45 V, 20 wt.% Ir on Vulcan XC-72). Moreover, the OER current density of $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid was explicitly higher than that of Co_3O_4 and N-PC over the whole potential range. The results confirmed that the presence of N-PC significantly enhanced the OER catalytic activity of Co_3O_4 in the hybrid, which in turn confirmed that the N-PC can be the active sites to boost OER. In the hybrid, the N-PC not only serve as a conduction path for shuttling electrons but also act as an active site for OER. Notably, the current density of commercial Ir/C even drops below that of $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid at potentials higher than 1.64 V, indicate that $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid is a highly active OER catalyst. The current density of 10 mA cm^{-2} , which is a metric relevant to solar fuel synthesis [53], can be achieved at a small potential of 1.62 V for our hybrid, The value is comparable to, or even better than those of other reported OER catalysts, including N-doped graphene/single-walled

carbon nanotube hybrid (1.63 V vs. RHE) [54], Nitrogen-doped graphene/CoSe₂ (1.60 V vs. RHE) [55], Mn₃O₄/CoSe₂ hybrid (1.68 V vs. RHE) [53], N-doped graphene/CNT composite (>1.65 V vs. RHE) [56], CaMn₄O_x (1.77 V vs. RHE) [57], rutile IrO₂ (1.68 vs. RHE) [58], and commercial Ir/C (1.60 vs. RHE, this work). Besides, the Co₃O₄/N-PC hybrid showed favorable kinetics toward OER with smaller Tafel slope of 72 mV/decade than those of Co₃O₄ (95 mV/decade) and N-PC (400 mV/decade) (Figure 4b). Importantly, the Tafel slope of hybrid is even smaller than that of commercial Ir/C (91 mV/decade), suggesting the outstanding intrinsic OER kinetics. Moreover, the Co₃O₄/N-PC hybrid exhibit much lower charge transfer resistance than Co₃O₄, as evidenced by the largely reduced diameter of the semicircle in the high-frequency region in the electrochemical impedance spectroscopy (EIS) profiles (Figure 2f). This result suggested a much smaller charge transfer resistance for the hybrid, due to the Co₃O₄-N-PC coupling that enhanced electron transport between Co₃O₄ and N-PC [59]. Catalyst durability is another major challenge for water splitting, and our hybrid exhibits durability superior to the Co₃O₄ catalyst, with little decay (4.4%) in OER activity up to 6,000 s of continuous operation at 1.7 V (Figure 4c), whereas the Co₃O₄ exhibited up to a 60.3% decrease in current density, suggesting a superior durability of the Co₃O₄/N-PC hybrid for OER. The results are most likely due to the fact that the Co₃O₄ nanoparticles were surrounded by N-PC (Figure 1), which can act as protective layers to stabilize Co₃O₄ nanoparticles [60, 61], and then make the Co₃O₄/N-PC hybrid more stable during OER testing. Further

stability test showed that the $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid almost afforded the same I-V curves as initial catalyst after 1,000 potential cycles, only with negligible drops of the anodic current (Figure 4d). The high stability of $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid was also observed in the chronoamperometric test, which showed insignificant current change after operation for near 10 h (Inset of Figure 4d). This current decrease may be caused by a small mass loss of the catalyst due to its partial peeling by a large amount of the evolved oxygen. Overall, such a high activity and stability of the hybrid may originate from the synergistic effect between Co_3O_4 and N-PC, as the N-PC can provide more active sites, enhance the electrical conductivity, and improve the stability of the hybrid as a protective layer.

Conclusions

In summary, we have demonstrated a facile method for synthesizing porous $\text{Co}_3\text{O}_4/\text{N-PC}$ dodecahedron hybrid. The electrochemical properties of the hybrid are characterized for both lithium storage and water splitting. It is demonstrated that the $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid with the combination of porous structure, highly conducting carbon networks, and well-dispersed Co_3O_4 nanoparticles delivers the best rate capability among all the Co_3O_4 -based anode materials up to now, i.e. a discharge capacity of as high as 560 mAh g^{-1} at 10 A g^{-1} , which is close to 46% of the rate capacity at 100 mA g^{-1} . In addition, the $\text{Co}_3\text{O}_4/\text{N-PC}$ hybrid also shows an excellent cycling stability with a 91.7% capacity retention of the second cycle after 110 cycles

and a considerably large discharge capacity of 1,730 mAh g⁻¹ at 100 mA g⁻¹. Furthermore, the hybrid also show enhanced electrocatalytic activity for electrochemical OER, thanks to the synergistic effects between the Co₃O₄ and N-PC. The promising results obtained in this study open up new avenues for the fabrication of other metal oxides/N-doped porous carbon hybrids, which may have potential applications in energy conversion and storage.

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Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version.

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Figure Captions

Figure 1. (a) Synthesis procedure and schematic diagram, (b) XRD pattern of $\text{Co}_3\text{O}_4/\text{N-PC}$, (c-d) TEM images, (e) HRTEM image, (f) FESEM and EDX mapping images of $\text{Co}_3\text{O}_4/\text{N-PC}$. Inset in (e) is corresponding SAED pattern.

Figure 2. (a) CV curves of $\text{Co}_3\text{O}_4/\text{N-PC}$, (b) Voltage profile of $\text{Co}_3\text{O}_4/\text{N-PC}$ at current density of 100 mA g^{-1} between 0.01 and 2.5 V over 100 cycles, (c) Cycle performance of all three samples tested at the same current density and voltage range, (d) Corresponding Coulombic efficiency curves of all three samples, (e) Rate performance of $\text{Co}_3\text{O}_4/\text{N-PC}$ between 0.01 and 2.5 V, and (f) Nyquist plots of Co_3O_4 and $\text{Co}_3\text{O}_4/\text{N-PC}$ in the frequency range between 100 KHz and 100m Hz.

Figure 3. FESEM images of ZIF-67 (a), $\text{Co}_3\text{O}_4/\text{N-PC}$ (b), and $\text{Co}_3\text{O}_4/\text{N-PC}$ after 100 charge/discharge cycles (c).

Figure 4. (a) Polarization curves and (b) corresponding Tafel plots of Co_3O_4 , $\text{Co}_3\text{O}_4/\text{N-PC}$, N-PC, and Ir/C at 5 mV s^{-1} in 0.1 M KOH solution. The IR drop was corrected. (c) Stability of current densities of Co_3O_4 and $\text{Co}_3\text{O}_4/\text{N-PC}$ at 1.7 V. (d) Polarization curves of $\text{Co}_3\text{O}_4/\text{N-PC}$ before and after 1,000 scan cycles at 5 mV s^{-1} . Inset in (d) is chronoamperometric response for $\text{Co}_3\text{O}_4/\text{N-PC}$ at 1.8 V.

Figure 1.

Figure 2.

Figure 3.

Figure 4.