Highly Active and Durable Nanocrystal-Decorated Bifunctional Electrocatalyst for Rechargeable Zinc–Air Batteries

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A highly active and durable bifunctional electrocatalyst that consists of cobalt oxide nanocrystals (Co$_3$O$_4$ NC) decorated on the surface of N-doped carbon nanotubes (N-CNT) is introduced as effective electrode material for electrically rechargeable zinc–air batteries. This active hybrid catalyst is synthesized by a facile surfactant-assisted method to produce Co$_3$O$_4$ NC that are then decorated on the surface of N-CNT through hydrophobic attraction. Confirmed by half-cell testing, Co$_3$O$_4$ NC/N-CNT demonstrates superior oxygen reduction and oxygen evolution catalytic activities and has a superior electrochemical stability compared to Pt/C and Ir/C. Furthermore, rechargeable zinc–air battery testing of Co$_3$O$_4$ NC/N-CNT reveals superior galvanodynamic charge and discharge voltages with a significantly extended cycle life of over 100 h, which suggests its potential as a replacement for precious-metal-based catalysts for electric vehicles and grid energy storage applications.

Introduction

With ever-increasing concerns over the depletion of fossil fuel, the development of next-generation energy conversion and storage systems has become the main focus to improve global sustainability. As natural sources of energy are non-renewable, systems that generate energy using these sources are likely to become obsolete and will eventually be replaced by advanced rechargeable energy systems based on renewable energy sources. Among a variety of rechargeable energy systems, the lithium ion battery (LIB) is one of the most widely used systems because its advantages such as high energy efficiency, high power density, and good cycle stability. [1] However, the limitations of the LIB for further development are its relatively low specific energy density, the high cost of active materials, and safety concerns particularly for electric vehicle (EV) and hybrid electric vehicle (HEV) applications. [1–3] However, advanced battery systems such as metal-air batteries (MABs), which utilize freely available oxygen in the atmosphere, have gained much attention recently because of their extremely high energy density, environmental benignity, low cost, and safe operation. [1–3] As they utilize oxygen from the atmosphere, MABs do not require fuel reservoirs that allows a lightweight and compact battery design and fabrication, which are highly desirable for extending the driving range of EVs and HEVs. Among MABs, lithium–air batteries (LABs) and zinc–air batteries (ZABs) have been investigated rigorously and have very high theoretical energy densities (11,680 and 1084 Wh kg$^{-1}$, respectively) [1,3,4] However, ZABs in particular have attracted tremendous attention because of their safe operation, easy handling, and the abundance of zinc sources. ZABs also are very attractive for EV applications, in which safe operation is important, because of the nonexplosive and nonflammable properties of their components. [2] Despite these advantages, a few technical challenges must be addressed before the widespread commercialization of ZABs because of their limited practical energy density and insufficient cycle life as well as some technical challenges. Among many components of MABs, the development of the air electrode is one of the most critical areas especially to make it efficiently rechargeable mainly because of the sluggish kinetics of oxygen electrochemical reactions involved during the battery operation. [1,4–9] To make MABs properly rechargeable, the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), which are fundamental electrode reactions that govern the overall battery operation, must be catalyzed by a bifunctional oxygen electrocatalyst. Therefore, the development of highly active, durable, and cost-effective bifunctional electrocatalysts for air electrodes is critical for the future implementation of this technology. To date, noble-metal-based catalysts such as Pt and Ir on carbonaceous support materials (Pt/C and Ir/C) are currently the best ORR and OER electrocatalysts, respectively [10–15] however, their severe scarcity, high prices, and insufficient electrochemical stability make them unsuitable for a wide range of practical applications.

To replace precious-metal-based catalysts, highly active and durable catalysts based on non-precious-metal or metal-free electrode materials have been developed. [12,14–24] For instance, Shanmugam et al. reported nanostructured 1D NiCo$_2$O$_4$ spinel...
The TEM image and XRD pattern of CoO\(_4\) NC, and SEM and TEM images of as-synthesized N-CNT are shown in Figure 1. The TEM image of CoO\(_4\) NC shows cube-shaped nanocrystals with an average size of 5 nm and a good particle size uniformity (Figure 1a). The XRD pattern of CoO\(_4\) NC is indicative of a cubic spinel crystal structure consistent with typical cobalt oxide nanoparticles (JCPDS no. 43–1003; Figure 1b).

The noise in the XRD pattern is caused by the very small dimensions of CoO\(_4\) NC, however, the main peaks characteristic of spinel CoO\(_4\) such as the (220), (331), and (511) reflections can still be observed. The SEM image of N-CNT reveals a uniformly grown tubular structure with a smooth outer surface that has an average diameter of ~50 nm and a length of several micrometers (Figure 1c). The TEM image of N-CNT supports the observations from the SEM image as bamboo-like structures are clearly visible that are attributed to defects at six-membered carbon rings in CNT (Figure 1d), which are generated by the five- and seven-membered ring construction because of the nitrogen dopants in the CNT. SEM, TEM, and scanning transmission electron microscopy (STEM) images with color mapping from energy-dispersive X-ray (EDX) analysis of the CoO\(_4\) NC/N-CNT hybrid are shown in Figure 2. In this work, our strategy to create a hybrid catalyst is based on the fast solvation-induced assembly of CoO\(_4\) NC/surfactant, which is attracted by a strong hydrophobic interaction onto the surface of N-CNT. The resulting hybrid shows CoO\(_4\) NC still distributed uniformly onto the surfaces of N-CNT even after the removal of the surfactant (Figure 2a). A high-magnification TEM image of a single N-CNT shows that its surface is decorated uniformly with CoO\(_4\) NC, and its bamboo-like morphology is also observed (Figure 2b). This hybrid material improves the morphology of CoO\(_4\) NC particles grown hydrothermally from seed onto the surfaces of undoped multiwalled CNT reported previously in our group. The formation of the unique morphology of the CoO\(_4\) NC/N-CNT hybrid in this work is attributed to the two-phase-induced CoO\(_4\) NC/surfactant system, which prevents aggregation and maintains the nanoscale particle size of the CoO\(_4\) NC. A high-resolution TEM (HR-TEM) image was obtained to further examine the crystallinity of CoO\(_4\) NC using a fast Fourier transform (FFT) pattern (Figure 2b inset), which demonstrates the highly crystalline spinel structure of CoO\(_4\) NC consistent with the XRD pattern. The adhesion of CoO\(_4\) NC onto the surface of N-CNT is verified by STEM, and the elemental distribution is obtained by EDX as shown in the color maps (Figure 2c–e). The dashed rectangular area of the N-CNT surface decorated with CoO\(_4\) NC resulted in purple-colored dots (Figure 2c). This shows the spread of cobalt oxide nanoparticles, which correspond to the small white particles (Figure 2d), and the yellow-colored dots show carbon species from N-CNT (Figure 2e). The yellow spots observed outside the rectangle are caused by the carbon-coated TEM copper grid.

CoO\(_4\) NC decorated on Vulcan carbon (CoO\(_4\) NC/VC), which is synthesized using the same method as CoO\(_4\) NC/N-CNT, was investigated using TEM and SEM. CoO\(_4\) NC/VC is employed as the control catalyst to elucidate the effect of the use of N-CNT.
as well as the synergistic effects between Co$_3$O$_4$ NC and N-CNT. It is also used to compare the morphological differences between the two respective carbon supports: N-CNT and VC (Figure S2). Similar to that of Co$_3$O$_4$ NC/N-CNT, Co$_3$O$_4$ NC are distributed well on the surface of VC articles. However, the VC particles themselves are observed to be aggregated, which reduces the overall exposure of active sites of Co$_3$O$_4$ NC. This is indicative of the effectiveness of N-CNT to enhance the exposure of the active sites of Co$_3$O$_4$ NC by creating an intertwined network because of its 1D morphology. The intertwined network of N-CNT has also been proven to be effective in terms of transporting charges during electrochemical oxygen reactions.$^{[14]}$
Thermogravimetric analysis (TGA) of $\text{Co}_3\text{O}_4\text{NC/N-CNT}$ was conducted in air to measure the amount of $\text{Co}_3\text{O}_4\text{NC}$ in the hybrid. A 45.7% weight reduction was observed over the temperature range of 300–450°C because of the decomposition of N-CNT (Figure S3). As N-CNT has been etched to remove the leftover Fe from the injection chemical vapor deposition (CVD) growth before hybridization with $\text{Co}_3\text{O}_4\text{NC}$, the amount of $\text{Co}_3\text{O}_4\text{NC}$ in the hybrid is determined to be 54.3%.

To further elucidate the elemental composition and catalytically active sites of the $\text{Co}_3\text{O}_4\text{NC/N-CNT}$ hybrid catalyst, X-ray photoelectron spectroscopy (XPS) was conducted. As expected, the full XPS survey of $\text{Co}_3\text{O}_4\text{NC/N-CNT}$ reveals peaks that correspond to Co 2p, Fe 2p, O 1s, N 1s, and C 1s (Figure 3a). The surface N content in N-CNT is confirmed to be 4.18%, which is consistent with CVD-grown N-CNT reported previously. The high-resolution N 1s spectrum of $\text{Co}_3\text{O}_4\text{NC/N-CNT}$ was deconvoluted into a series of four peaks, which match the binding energies of different N-containing species such as pyridinic, pyrrolic, quaternary, and pyrrolidone closely (Figure 3b). The two species with the highest quantity, namely, pyridinic and pyrrolic, are 42.2 and 23.7% of the total, respectively. These ratio and binding energies of the surface N groups are consistent with N-CNT reported previously. Among the four different N species, pyridinic and quaternary nitrogen species serve as the active site for the ORR.

This is appealing for combination with a highly active OER electrocatalyst such as $\text{Co}_3\text{O}_4\text{N}$ to obtain a highly efficient bifunctional air electrode catalyst. The high-resolution Co 2p spectrum of the hybrid material has been deconvoluted into a series of six peaks, which are consistent with results reported previously (Figure S4).

ORR polarization curves of $\text{Co}_3\text{O}_4\text{NC/N-CNT}, \text{Co}_3\text{O}_4\text{NC/VC},$ and N-CNT are shown in Figure 4a. Among the three, $\text{Co}_3\text{O}_4\text{NC/N-CNT}$ shows the most positive half-wave potential as well as the lowest overpotential, which are indicative of high electrochemical catalytic activity towards the ORR. Although $\text{Co}_3\text{O}_4\text{NC/N-CNT}$ has a lower N-CNT loading than N-CNT (because the total loading is kept the same), $\text{Co}_3\text{O}_4\text{NC/N-CNT}$ shows significantly improved onset and half-wave potentials. Even though the ORR of $\text{Co}_3\text{O}_4\text{NC/N-CNT}$ proceeds through the four-electron pathway, as determined by Koutecky–Levich (K-L) analysis (below), the slightly lower limiting current density obtained with $\text{Co}_3\text{O}_4\text{NC/N-CNT}$ than that of N-CNT is likely because of nonideal factors in the catalyst-coated layer on the glassy carbon such as film thickness resistance and trapped hydrogen.
peroxide species formed by the ORR catalyzed on CoO$_2$ NC within the electrode.$^{[38,39]}$ The combination of CoO$_2$ NC with N-CNT through hydrophobicity-induced coupling results in a superior ORR activity and signifies a strong synergistic effect between the two materials. CoO$_2$ NC/VC combined by the same method as CoO$_2$ NC/N-CNT lacks a significant ORR activity based on the considerably negative onset and half-wave potentials and reduced limiting current density. To investigate the bifunctionality of CoO$_2$ NC/N-CNT, the OER activity was investigated by cyclic voltammetry (CV) in the voltage range of 0–1 V vs. the saturated calomel electrode (SCE; Figure 4b). Of the three materials tested, the hybrid catalyst shows the best ORR activity demonstrated by the highest OER current density of 42 mA cm$^{-2}$ obtained at 1.0 V. Furthermore, CoO$_2$ NC/N-CNT shows the lowest overpotential of 0.802 V vs. SCE obtained at 20 mA cm$^{-2}$. Even though CoO$_2$ NC/VC demonstrates the same onset potential (~0.57 V vs. SCE), the OER current density at 1.0 V is only 35 mA cm$^{-2}$. The OER and ORR activities of the three catalysts are summarized in Table S1. The synergistic combination of CoO$_2$ NC and N-CNT by hydrophobicity-induced coupling is again demonstrated for the OER, in which N-CNT shows a poor onset potential and a low current density. With the addition of CoO$_2$ NC, the OER onset potential and current density were improved significantly. The two materials are synthesized from the same CoO$_2$ NC and are utilized as OER-active electrocatalysts. However, due to different natures of carbon supports utilized, VC leads to the decrease in exposed active sites for OER, whereas N-CNT enhances overall electrical conductivity by acting as a bridge for electron transfer and increases active site exposure for improved OER.

To further understand the excellent ORR kinetics of the CoO$_2$ NC/N-CNT hybrid catalyst, K-L analysis was conducted at various electrode potentials (0.65, 0.70, 0.75, and 0.80 V; Figure 4d) based on the Koutecky–Levich equation (Supporting Information) using OER measurements obtained by using a RDE at four different rotation speeds of 400, 900, 1600, and 2500 rpm (Figure 4c). These parallel and linear fitting lines indicate first-order reaction kinetics towards the saturated oxygen species. The number of electrons transferred, $n$, during the ORR is 3.9, 3.9, 4.0, and 4.0 at potentials of 0.65, 0.70, 0.75, and 0.80 V vs. SCE, respectively. This indicates fast kinetics with a predominant four-electron reduction reaction mechanism throughout the entire potential range inspected. This high activity towards the ORR is attributed to the synergy between CoO$_2$ NC and N-CNT, and the coupling of the two by strong hydrophobic interactions improved the active surface area and charge transport properties. To emphasize the potential use of CoO$_2$ NC/N-CNT hybrid catalyst for practical applications, its ORR and OER activities are compared to those of commercial state-of-the-art catalysts, Pt/C and Ir/C (Figure S5a and b, respectively). As Pt/C and Ir/C are known to be monofunctionally active towards the ORR and OER, respectively, the two were mixed physically in a 1:1 ratio to create a bifunctional-ly active counterpart. The ORR measurements of the catalysts reveal that even though the mixture of Pt/C and Ir/C outperforms CoO$_2$ NC/N-CNT slightly in terms of onset and half-wave potentials and limiting current density, the cost effectiveness of the hybrid catalyst compensates for the sacrificed performance. Similarly, the OER activity of the mixture of Pt/C and Ir/C outperforms that of CoO$_2$ NC/N-CNT slightly in terms of onset potential and OER current density. The ORR and OER activities of the composite can be further enhanced by introducing a second transition metal such as NiCo$_2$O$_4$ and the co-doping of carbon nanotubes, such as S,N-doped carbon nanotubes, to outperform Pt/C and Ir/C, which will be investigated in our future work.

In addition to the ORR and OER activities of CoO$_2$ NC/N-CNT, the electrochemical durability of the hybrid catalyst has been investigated to further highlight its potential application in practical rechargeable metal–air batteries (Figure 5). The electrochemical durability is tested by conducting repeated CVs in the range of 0–1 V vs. SCE to expose the catalyst to severely oxidative conditions. Even after 1000 cycles, the CoO$_2$ NC/N-CNT hybrid catalyst shows a relatively low decrease in current density at 1 V vs. SCE (Figure 5a), whereas CoO$_2$ NC/VC, N-CNT, and the mixture of Pt/C and Ir/C demonstrate a significant reduction in current density (N-CNT only after 300 cycles; Figure 5b, c, and d Table S1). Even though CoO$_2$ NC helps to reduce the overpotential associated with OER for both the N-CNT- and VC-supported hybrids, CoO$_2$ NC/N-CNT demonstrates a much higher current density retention (91.2%) than CoO$_2$ NC/VC (40.7%) because of the graphitized carbon in N-CNT, which is known to be electrochemically very
In addition, the improved durability is ascribed to the morphological advantage of the highly intertwined network of 1D carbon nanotubes over the granular morphology created by VC.\textsuperscript{[18]} Although the mixture of Pt/C and Ir/C shows superior initial activity to Co\textsubscript{3}O\textsubscript{4} NC/N-CNT, it demonstrates a poor durability, which highlights the hybrid catalyst as a potential replacement for practical applications. The decrease of current density for Pt/C and Ir/C is most likely attributed to the corrosion of carbon during exposure to high charging potentials, however, Co\textsubscript{3}O\textsubscript{4} NC/N-CNT is significantly less affected because of the synergistically enhanced catalytic activity, which prevents N-CNT from prolific corrosion.\textsuperscript{[1, 14, 18]}

To corroborate the excellent bifunctional activities of Co\textsubscript{3}O\textsubscript{4} NC/N-CNT confirmed by half-cell testing, a rechargeable zinc–air cell prototype was fabricated, and the hybrid material was tested as the air electrode catalyst to emphasize its electrocatalytic performance in a realistic environment. The zinc–air battery performance of the catalysts was investigated by conducting galvanodynamic charge and discharge tests to observe the behavior of battery operation in terms of voltage for a wide range of applied (or drawn) current densities (Figure 6a). The open-circuit voltages of Co\textsubscript{3}O\textsubscript{4}/N-CNT and N-CNT are comparable and higher than that of Co\textsubscript{3}O\textsubscript{4} NC/VC because of the superior electrical conductivity of the CNT. In terms of discharge, Co\textsubscript{3}O\textsubscript{4} NC/N-CNT demonstrates the best discharge performance as evidenced by the highest discharge voltages obtained at all tested current densities. The differences in the discharge voltage become clearer at high current densities, which is indicative of the superior rate capability of Co\textsubscript{3}O\textsubscript{4} NC/N-CNT. The trend in the observed discharge performance is consistent with that of the half-cell testing in which N-CNT shows a better performance than Co\textsubscript{3}O\textsubscript{4} NC/VC, most likely because of the fast charge transport facilitated by the highly electrically conductive CNT. During battery charging, Co\textsubscript{3}O\textsubscript{4} NC/N-CNT demonstrates best overall OER performance with significantly lower charging potentials particularly at high current densities.

In addition to the galvanodynamic charging and discharging behaviors of the catalysts, electrochemical impedance spectroscopy (EIS) was conducted in the ORR region at 0.8 V to further investigate the resistances associated with rechargeable zinc–air battery operation (Figure 6b, inset). EIS testing resulted in Nyquist plots composed of two different sized semicircles, which are modeled by an equivalent circuit with five parameters, $R_s$, $R_{int}$, $R_{ct}$, $Q_{int}$, and $Q_{dl}$, consistent with our zinc–air battery results reported previously.\textsuperscript{[14, 18, 37]} Each resistance has its own physical interpretation. $R_s$ represents solution resistance in the electrolyte, and $R_{int}$ represents...
solid–electrolyte interface resistance between the solid and liquid of the electrode. $R_e$ represents charge-transfer resistance from the air electrode, which is related directly to the catalytic activity of the catalyst. $Q_{ct}$ and $Q_{dl}$ correspond to interfacial and double layer constant phase elements (CPEs), respectively. Based on the equivalent circuit, the impedance parameters of each catalyst are listed in Table 1, and Co$_3$O$_4$ NC/N-CNT exhibits a lower charge-transfer resistance than Co$_3$O$_4$ NC/VC and N-CNT, which is consistent with the results obtained from the galvanodynamic discharge test. The hybrid also presents the lowest values of $R_e$ and $R_{int}$, which is because of the addition of soning of the electrolyte, which results in the loss of discharge voltages. The rate of charge voltage loss is more severe for Co$_3$O$_4$ NC/VC than N-CNT because of the amorphous nature of VC, whereas the graphitic carbon of N-CNT mitigates the rate of degradation. Similarly, the mixture of Pt/C and Ir/C demonstrates severe degradation in terms of both charge and discharge voltages even though its initial performance is superior. Furthermore, the initial four cycles of the charge–discharge profiles of Co$_3$O$_4$ NC/VC, N-CNT, and the mixture of Pt/C and Ir/C demonstrate high overpotentials, whereas Co$_3$O$_4$ NC/N-CNT shows a relatively narrow difference between the charge–discharge voltages (inset in Figure 7b, 7, and d, respectively). This galvanostatic cycling test is indicative of the importance to have both stable graphitic carbon and highly OER-active Co$_3$O$_4$ NC to minimize charge–discharge voltage degradation. To further confirm the durability of the hybrid catalyst, a long-term galvanostatic charge–discharge cycling test was conducted using a 4 h cycling interval (2 h discharge then 2 h charge) at the same current density (Figure 8). Even though this leads to harsh testing conditions for the catalyst in terms of electrochemical durability, the battery exhibits very stable voltages over 100 h (350 000 s). This result obtained with long charging and discharging regimes demonstrates the potential use of the highly active and durable Co$_3$O$_4$ NC/N-CNT hybrid bifunctional catalyst as an efficient air electrode material for real applications.

### Table 1. Values of the equivalent circuit elements based on the EIS analysis of Co$_3$O$_4$ NC/N-CNT, Co$_3$O$_4$ NC/VC, N-CNT, and a mixture of Pt/C and Ir/C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial cycle</th>
<th>After cycling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_e$ [\Omega]</td>
<td>$R_{int}$ [\Omega]</td>
</tr>
<tr>
<td>Co$_3$O$_4$ NC/N-CNT</td>
<td>1.849</td>
<td>0.199</td>
</tr>
<tr>
<td>Co$_3$O$_4$ NC/VC</td>
<td>2.116</td>
<td>0.284</td>
</tr>
<tr>
<td>N-CNT</td>
<td>1.887</td>
<td>0.264</td>
</tr>
<tr>
<td>Pt/C+Ir/C</td>
<td>1.954</td>
<td>0.236</td>
</tr>
</tbody>
</table>

Figure 7. Galvanostatic charge–discharge cycling obtained at 20 mA cm$^{-2}$ for (a) Co$_3$O$_4$ NC/N-CNT, (b) Co$_3$O$_4$ NC/VC, (c) N-CNT, and (d) Pt/C+Ir/C. Insets: The initial four cycles of each catalyst.
static cycling tests, the same batteries were tested for galvano-
dynamic charge and discharge to further verify the durability of
the catalysts (Figure S6a and c). Co$_3$O$_4$/N-CNT suffers from
the largest charge and discharge performance loss compared
to its initial performance observed by the greater increase
in charge and discharge overpotentials. The Co$_3$O$_4$/N-CNT
hybrid catalyst shows the smallest decrease and increase in
the discharge and charge voltage, respectively, which eluci-
dates the electrochemical stability with highly active bifunc-
tional properties. The bifunctional mixture of Pt/C and Ir/C also
displays a considerably enlarged charge/discharge voltage dif-
ference in contrast to that of the hybrid material. The order of
the increased overpotential between the charge and discharge
profiles from that at the initial stage is Co$_3$O$_4$/N-CNT < N-
CNT < Pt/C-Ir/C < Co$_3$O$_4$/N-CNT, which corresponds to 0.297,
0.501, 0.883, and 1.126 V, respectively, at a relatively high cur-
cent density of 50 mA cm$^{-2}$ (Tables S2 and S3). With respect to
electrochemical resistances in the zinc–air battery single cell,
EIS was conducted at the last stage after charge–discharge cy-
ing experiments as displayed by the Nyquist plots (Fig-
ure S6b and d). In agreement with the trend of the increasing
overpotentials before and after the galvanostatic charge and
discharge cycling test, the increase in the electrochemical resis-
tances is observed in the order of Co$_3$O$_4$/N-CNT < pure N-
CNT < Pt/C-Ir/C < Co$_3$O$_4$/N-CNT. Conclusively, all of electro-
chemical characterizations such as half-cell testing, galvano-
dynamic and galvanostatic charge and discharge, and EIS demon-
strate a consistent durability trend among the catalysts. In com-
parison with the other electrocatalysts, Co$_3$O$_4$/N-CNT has a strong electrochemical durability and excellent recharge-
ability as well as a highly active and bifunctional performance
in both half-cell testing and zinc-air battery cycling experi-
ments.

Conclusions

A facile synthesis method to decorate cobalt oxide nanocrys-
tals (Co$_3$O$_4$/N-CNT) on the surface of N-doped carbon nanotubes
(N-CNT) is introduced based on hydrophobicity-induced solva-
tion to obtain a highly active Co$_3$O$_4$/N-CNT hybrid electro-
catalyst. The catalyst is formed by the strong hydrophobic in-
teractions between surfactants that encapsulate the Co$_3$O$_4$/N-CNT
and the graphitic walls of the N-CNT. From rotating disk elect-
trode half-cell testing and practical rechargeable zinc-air bat-
tery measurements, the synergistic effect of the Co$_3$O$_4$/N-
CNT hybrid catalyst is verified by comparing it to Co$_3$O$_4$/N-CNT
and N-CNT, which demonstrate relatively lower bifunctional ac-
tivities. The oxygen reduction reaction (ORR) and oxygen evolu-
tion reaction (OER) activity of the hybrid catalyst compared to
those of precious-metal-based catalysts such as Pt/C and Ir/C,
respectively, highlights its potential for usage in practical ap-
lications. The synergistic effect is obtained from the hydro-
phobic combination between N-doped CNT, which mainly pro-
vides highly active ORR sites and the exceptional electrical
conductivity for rapid charge transfer, and Co$_3$O$_4$/NC, which
provides highly exposed OER active sites. In addition to the
high bifunctional activity, Co$_3$O$_4$/N-CNT exhibits remarkably
stable OER polarization curves at a very high potential range
between 0 and 1 V (vs. standard calomel electrode) and sus-
tains more than 90% in OER current retention even after 1000
cyclic voltammetry cycles. The practicality of the hybrid cata-
lyst is further elucidated by its excellent cycling durability as
well as the low overpotential between charge and discharge
performances in a realistic rechargeable zinc–air battery under
ambient conditions. As a result of the simple and facile synthe-
sis of the nanocrystals with N-CNT, the Co$_3$O$_4$/N-CNT hybrid
catalyst is highly promising for next-generation rechargeable
batteries such as metal–air batteries and alkaline full cells.

Experimental Section

Chemicals and materials

All of chemicals were purchased from Sigma–Aldrich and used
without further processing. Cobalt nitrate hexahydrate, sodium
stearate, methanol, tolulene, dodecylamine, and tert-butylamine
were employed for the synthesis of Co$_3$O$_4$/NC, ethylenediamine
and ferrocene were utilized for N-CNT, and sulfuric acid was used
to etch the N-CNT.

Catalyst preparation

Synthesis of N-CNT: N-CNT were prepared by a simple injection
CVD method as described previously. Briefly, ethylenediamine
(EDA) and ferrocene were employed as the carbon source and cat-
alyst, respectively. First, EDA and ferrocene were dissolved in etha-
nol by ultrasonication for 2 h to obtain a homogeneous dispersion.
Then, a tube furnace was set up with a large quartz tube, a syringe
pump, and a syringe, which was filled with EDA solution (2 mL).
The furnace was heated to 700 °C at which point the syringe pump
was turned on to begin injecting the precursor solution for 40 min
with a flow rate of 0.05 mL min$^{-1}$. Once the injection was finished,
the pump was turned off and the furnace was cooled to RT after
heating at 700 °C for total of 2 h. N-CNT was obtained by collecting
black powder from the quartz tube. N-CNT was then acid-treated
in 0.5 M H$_2$SO$_4$ solution to remove impurities including Fe particles.
After acid etching, N-CNT were washed and filtered using doubly
dionized (DDI) water and dried at 60 °C.

Synthesis of Co$_3$O$_4$/NC: Co$_3$O$_4$/NC were prepared by a simple two-
phase hydrothermal synthesis. Cobalt stearate (Co(SA)$_2$), which
was used as a precursor, was first prepared for synthesis of Co$_3$O$_4$
NC. In a typical synthesis, an oil-phase mixture of toluene (15 mL),
dodecylamine (1.0 g), and Co(SA)$_2$ (0.15 g) in a vial was heated at
90 °C until the solution become optically clear. Then the solution

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Figure 8. Long-term galvanostatic charge–discharge cycling obtained at
20 mA cm$^{-2}$ for Co$_3$O$_4$/N-CNT. Each charge and discharge state was 2 h
(4 h per cycle).

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**Figure 8.** Long-term galvanostatic charge–discharge cycling obtained at
20 mA cm$^{-2}$ for Co$_3$O$_4$/N-CNT. Each charge and discharge state was 2 h
(4 h per cycle).
was cooled to RT and loaded into a 50 mL Teflon liner. Deionized water (15 mL) and tert-butylamine (150 µL) were mixed to prepare a water-phase solution, which was added to the 50 mL Teflon liner before the addition of the oil-phase solution. The two-phase solution was heated in the autoclave without stirring at 180 °C for 5 h. After the autoclave reaction was finished and cooled to RT, the solution that contained Co₃O₄ NC was poured from the Teflon liner into a test tube and mixed with methanol (30 mL) to induce the precipitation of Co₃O₄ NC. Finally, Co₃O₄ NC were separated by centrifugation and washing with methanol solution and stored in a toluene solution, which was utilized as a redispersion agent for Co₃O₄ NC because of its hydrophobic properties.

Preparation of Co₃O₄ NC/N-CNT: Simple self-assembly was employed to obtain the hybrid catalyst.[44] As-prepared N-CNT were first dispersed into the Co₃O₄ NC solution under ultrasonication for 2 h. Then methanol was added into the mixture, which created a strong hydrophobic interaction between the two components that thereby self-assembled into the Co₃O₄ NC/N-CNT hybrid. The precipitated composite was separated by vacuum filtration and dried completely at 50 °C. Finally, the dried composite was heat treated at 450 °C for 2 h under Ar to obtain strong coupling between Co₃O₄ NC and N-CNT and eliminate any remaining surfactants between the two components. Co₃O₄ NC/VC employed as a reference material was prepared using vulcan carbon (Vulcan XC-72) instead of the N-CNT from the same synthesis. The overall synthesis of Co₃O₄ NC, N-CNT, and Co₃O₄ NC/N-CNT is illustrated in Scheme 1b.

Materials characterization

For chemical and physical characterization of the prepared materials, a variety of techniques were employed. SEM (LEO FESEM 1530) and TEM (JEOL 2010F) images were obtained to investigate the surface structure and morphology of the prepared materials. Furthermore, HR-TEM, selected area electron diffraction (SAED), STEM, and color mapping based on EDX were employed to identify the nanocrystals as spinel cobalt oxide and to study their crystallinity in Co₃O₄ NC/N-CNT. XRD (Bruker AXS D8 Advance) was utilized to confirm the spinel crystal structure of cobalt oxide nanocrystals in Co₃O₄ NC/N-CNT, and XPS (Thermal Scientific K-Alpha XPS spectrometer) was implemented not only to verify the surface atomic composition of the developed material, but also to quantify the different configurations of nitrogen species. TGA was performed to elucidate the amount of Co₃O₄ NC in the hybrid.

Preparation of a glassy carbon electrode

A glassy carbon electrode (Diameter: 5 mm with surface area: 0.196 cm²) was utilized as a working electrode. It was first polished by using alumina powder (size: 0.3 µm and 0.05 µm), and then the electrode was ultrasonicated directly in deionized water for a short time then dried in a nitrogen gas stream. To prepare the sample ink, the catalyst (4 mg) was put into ethanol (1 mL) pretreated by Nafion solution (0.05 wt%), and the mixture was ultrasonicated for 2 h to obtain a homogeneously mixed ink. The as-prepared dispersion (20 µL) was dropped onto the circle-shaped glassy carbon and dried under ambient conditions (catalyst loading: 0.4 mg cm⁻²).

Electrochemical measurements: Three-electrode half-cell testing

A RDE half-cell system was employed to investigate both the ORR and OER catalytic activity of the prepared materials. A conventional three-electrode system that consisted of a working electrode, counter electrode, and reference electrode was used. As described above, the catalyst-coated glassy carbon disk electrode and a Pt wire were used as the working and counter electrodes, respectively, and a SCE was employed as the reference electrode. KOH solution (0.1 M) was used as the aqueous electrolyte. To obtain an O₂ or N₂-saturated electrolyte, O₂ or N₂ was used to purge the KOH solution for 30 min before the evaluations, and bubbling was continued during the tests. The electrochemical activities of the materials were studied by CV for the OER and linear sweep voltammetry (LSV) for the ORR, which were performed by using a CHI Electrochemical Station (Model 760D) and a rotation speed controller (Pine Instrument Co., AFCBP-1). Catalytic activity towards the ORR was recorded from 0.1 to −1.0 V vs. SCE at a scan rate of 10 mV s⁻¹ with O₂-saturated electrolyte under a series of rotating electrode speeds (400, 900, 1600, and 2500 rpm). The ORR polarization curves were corrected by subtracting background currents by the same test procedures obtained with a N₂-saturated electrolyte to remove capacitive contributions during the tests of ORR activities. The electrochemical performance of the OER was evaluated from 0−1 V vs. SCE at a scan rate of 10 mV s⁻¹ (50 mV s⁻¹ for the ORR cycling as a durability test) with N₂-saturated electrolyte at 900 rpm to remove surface O₂ bubbles generated during the OER test. The precious-metal-based bifunctional active material that consisted of both Pt/C (28.8 wt% Pt), as one of the best ORR electrocatalysts, and Ir/C (20 wt% Ir), as one of the best OER catalysts, was employed as the reference material to demonstrate the superiority of the bifunctional Co₃O₄ NC/N-CNT hybrid material.

Fabrication of zinc–air battery single cell and performance evaluation

The practical use of the electrochemical catalyst was investigated by using a rechargeable zinc–air battery (ZAB) prototype, which consisted of an air electrode, zinc plate, electrolyte, and separator (Supporting Information, Figure S1). The air electrode was first prepared using a gas diffusion layer (GDL; Ion Power Inc., SGL Carbon 10 BB) upon which the catalyst was spray-coated by using an air brush with an air electrode active area of 0.785 cm².[34] The catalyst materials were dispersed in a Nafion-containing (5 wt%) isopropanol mixture with a catalyst concentration of 4 mg mL⁻¹. This mixture was then ultrasonicated for 1 h at RT to obtain a well-dispersed ink solution. Then, it was air-brush sprayed onto the GDL for subsequent testing (average catalyst/binder loading: 1 mg cm⁻²). A polished zinc plate (OnlineMetals, Zinc Sheet EN 988), a microporous 25 µm polypropylene membrane (Celgard 5550), and 6.0 M KOH with 0.2 M zinc acetate solution were employed as the anode, separator, and electrolyte, respectively. Galvanodynamic discharge and charge experiments and EIS tests were performed by using a multichannel potentiostat (Princeton Applied Research, VersaSTAT MC). Discharge and charge profiles were obtained at a wide range of current change (current density: 0−60 mA cm⁻²). The EIS was implemented with a fixed potential at 0.8 V and the frequency was changed from 100 000 to 0 Hz. All of the tests were conducted before and after cycles. Zinc–air battery single-cell cycling tests were performed by using a cycling tester (BTSDA). The cycling was performed with 10 min cycles (5 min discharge and 5 min charge) and a high current density of
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