Size-Dependent Activity Trends Combined with in Situ X-ray Absorption Spectroscopy Reveal Insights into Cobalt Oxide/Carbon Nanotube-Catalyzed Bifunctional Oxygen Electrocatalysis

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S Supporting Information

ABSTRACT: Bifunctional oxygen electrocatalysts play a vital role in important energy conversion and storage devices. Cost-effective, abundant, and active Co-based materials have emerged as promising bifunctional electrocatalysts for which identifying catalytically active structures under reaction conditions and unraveling the structure−activity relationships are of critical importance. Here, we report the size-dependent (3−10 nm) structure and catalytic activity of bifunctional cobalt oxide nanoparticle (CoOx NP) catalysts for the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR). In situ X-ray absorption spectroscopy (XAS) revealed that the majority of NPs during OER and ORR were composed of the Co3O4 and CoOOH phases regardless of their particle sizes. The OER activity increased with decreasing NP size, which correlated to the increased oxidation state and larger surface area in smaller NPs, whereas the ORR activity was nearly independent of NP size. These particle size-dependent catalytic activities in conjunction with the in situ XAS results can provide insights into the CoOx-catalyzed bifunctional oxygen electrode reactions.

KEYWORDS: cobalt oxide, size effect, bifunctional catalysis, oxygen evolution reaction, oxygen reduction reaction

With increasing demand for clean energy technologies, renewable energy conversion and storage systems have generated tremendous interest.1,2 Bifunctional oxygen electrocatalysts that can catalyze both oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are ubiquitous and of pivotal importance in energy devices, such as unitized regenerative fuel cells and metal−air batteries.3−12 The viability of these energy devices is critically dependent on the catalytic performances of bifunctional oxygen electrocatalysts. Both OER and ORR involve the transfer of four electrons, rendering these reactions energetically demanding and sluggish. As such, noble metal-based materials like IrO2, RuO2, and Pt with fast reaction kinetics have been used prevalently as bifunctional electrocatalysts; however, they are costly and scarce.13,14 In this context, cost-effective and abundant transition metal oxides and hydroxides have emerged as a promising class of catalysts.15−24 Cobalt oxide-based bifunctional electrocatalysts have been of particular interest as economically viable and efficient bifunctional oxygen electrocatalysts.16−19,22−24

For the design of advanced cobalt oxide-based electrocatalysts, unraveling the nature of the active species and reaction mechanism is of critical importance, and understanding the nanoscale particle size effects can provide important clues. The particle size effects in cobalt (oxide)-based catalysts have been established in a number of important reactions, including Fischer−Tropsch synthesis and CO2 hydrogenation.25,26 However, such insights have not yet been gained for bifunctional oxygen electrocatalysis; only a few sporadic works on the size dependency for respective OER or ORR have been reported.27,28 More importantly, an understanding of the size-dependent catalytic activity in symbiosis with in situ spectroscopic characterization can further provide more compelling evidence to establish the property relation...
ships between structure (size, shape, and/or composition) and catalysis.\(^{29}\)

Herein, we report the nanoscale size-dependent structure and catalytic activity of bifunctional electrocatalysts based on cobalt oxide nanoparticles (CoO\(_x\) NPs) for both OER and ORR for the first time. CoO\(_x\) NPs with four different particle sizes, tunable from 3 to 10 nm, were synthesized and deposited on acid-treated carbon nanotubes (CNTs), according CoO\(_x\)/CNTs model catalysts to investigate bifunctional electrocatalysis in alkaline media. In situ X-ray absorption spectroscopy (XAS) analysis revealed that the composition of the size-controlled CoO\(_x\) NPs was invariably Co\(_3\)O\(_4\) and CoOOH with a small amount of Co(OH)\(_2\) under electrochemical OER and ORR conditions. This result suggests that Co(III) species are the key elements for OER, whereas they appear to be side products generated from the oxidation of Co(II) by a peroxide intermediate during ORR. The CoO\(_x\)/CNT catalysts exhibited increasing OER activity with decreasing NP size, which could be correlated with abundant surface Co(III) species and the large surface area of small CoO\(_x\) NPs. For ORR, no particle size dependence was found in the kinetic region; CoO\(_x\) NPs mainly played an auxiliary role, promoting the reduction or disproportionation of peroxide generated from the two-electron transfer pathway of the ORR.

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**RESULTS AND DISCUSSION**

Preparation of the CoO\(_x\)/CNTs model catalysts consisted of (i) the colloidal synthesis of CoO\(_x\) NPs with different particle sizes,\(^{26}\) (ii) the attachment of prepared NPs to acid-treated CNTs, and (iii) mild annealing to remove residual organic surfactants around the CoO\(_x\) NPs. Monodisperse, size-controlled CoO\(_x\) NPs with average sizes of 3.0, 6.2, 7.4, and 9.1 nm were obtained by controlling thermal decomposition temperature of precursor (Table S1 and Figure S1). High-resolution TEM (HR-TEM) images (Figure S1e\(\rightarrow\)h) demonstrated that all of the NPs consisted of the crystalline CoO phase (cubic, \(a = 4.22\) Å).

CoO\(_x\) NPs were then anchored onto the acid-treated CNTs with ultrasonication, followed by mild thermal annealing. We chose undoped CNTs rather than N-doped CNTs as the support material because the presence of both CoO\(_x\) and nitrogen synergistically enhances catalytic activity via the formation of Co–N bonding, potentially hampering the extraction of catalytic activity exclusively from CoO\(_x\).\(^{16,30,31}\) The nominal content of Co in the CoO\(_x\)/CNTs was around 12 wt %, as confirmed by inductively coupled plasma optical emission spectrometry (Table S1). Scanning electron microscopy (SEM) images (Figure S2) of the CoO\(_x\)/CNTs revealed the preserved morphology after the loading of the CoO\(_x\) NPs.

Figure 1. Characterizations of the CoO\(_x\)/CNTs. (a–d) BF-TEM images of (a) CoO\(_x\)(4.3)/CNTs, (b) CoO\(_x\)(6.3)/CNTs, (c) CoO\(_x\)(7.5)/CNTs, and (d) CoO\(_x\)(9.5)/CNTs. (e–h) Corresponding AR-TEM images and FFT patterns (insets). (i) Histograms of the particle size distributions of the CoO\(_x\) NPs.
X-ray diffraction (XRD) patterns (Figure 2a) of all the samples showed a common diffraction peak at $2\theta = 25.7^\circ$ coincident with those that appeared for the CNTs. The diffraction peaks at $2\theta = 36.5^\circ$, $42.8^\circ$, and $61.5^\circ$ were commensurate with those of the CoO standard appeared in CoO$_x$(6.3)/CNTs, CoO$_x$(7.5)/CNTs, and CoO$_x$(9.5)/CNTs.

Table 1. Phase Composition and Average Co Oxidation State of the CoO$_x$ NPs in the CoO$_x$/CNTs As Determined by Linear Combination Fitting of the In Situ XANES at OCV, 1.8 V, and 0.6 V (vs RHE)

<table>
<thead>
<tr>
<th>sample</th>
<th>condition</th>
<th>Co$_3$O$_4$</th>
<th>CoOOH</th>
<th>CoO</th>
<th>Co(OH)$_2$</th>
<th>average Co oxidation state</th>
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<tr>
<td>CoO$_x$(4.3)/CNTs</td>
<td>OCV</td>
<td>0.61</td>
<td>0.20</td>
<td>0.00</td>
<td>0.19</td>
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<tr>
<td></td>
<td>1.8 V</td>
<td>0.55</td>
<td>0.42</td>
<td>0.01</td>
<td>0.02</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>0.6 V</td>
<td>0.26</td>
<td>0.56</td>
<td>0.00</td>
<td>0.18</td>
<td>2.8</td>
</tr>
<tr>
<td>CoO$_x$(6.3)/CNTs</td>
<td>OCV</td>
<td>0.32</td>
<td>0.15</td>
<td>0.18</td>
<td>0.35</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>1.8 V</td>
<td>0.54</td>
<td>0.41</td>
<td>0.03</td>
<td>0.02</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>0.6 V</td>
<td>0.20</td>
<td>0.65</td>
<td>0.00</td>
<td>0.17</td>
<td>2.8</td>
</tr>
<tr>
<td>CoO$_x$(7.5)/CNTs</td>
<td>OCV</td>
<td>0.19</td>
<td>0.30</td>
<td>0.09</td>
<td>0.43</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>1.8 V</td>
<td>0.44</td>
<td>0.50</td>
<td>0.00</td>
<td>0.06</td>
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<tr>
<td></td>
<td>0.6 V</td>
<td>0.44</td>
<td>0.50</td>
<td>0.00</td>
<td>0.06</td>
<td>2.8</td>
</tr>
<tr>
<td>CoO$_x$(9.5)/CNTs</td>
<td>OCV</td>
<td>0.00</td>
<td>0.47</td>
<td>0.00</td>
<td>0.53</td>
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</tr>
<tr>
<td></td>
<td>1.8 V</td>
<td>0.29</td>
<td>0.49</td>
<td>0.00</td>
<td>0.22</td>
<td>2.7</td>
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<tr>
<td></td>
<td>0.6 V</td>
<td>0.57</td>
<td>0.22</td>
<td>0.07</td>
<td>0.14</td>
<td>2.6</td>
</tr>
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</table>
In the case of the CoO\textsubscript{x}(4.3)/CNTs, different diffraction peaks (2\(\theta\) = 31.8°, 36.8°, 44.9°, 59.4°, and 65.2°) were observed and could match those of the Co\(_3\)O\(_4\) standard. The radial distribution function (RDF) from Fourier transform of \(k^2\)-weighted extended X-ray absorption fine structure (EXAFS) spectrum (Figure 2b) of CoO\(_x\)(4.3)/CNTs exhibited major peaks at 1.54, 2.48, and 3.06 Å corresponding to the Co–O, Co\(_{\text{oct}}\)–Co\(_{\text{oct}}\), and Co\(_{\text{tet}}\)–Co\(_{\text{tet}}\) pairs of Co\(_3\)O\(_4\), respectively.\(^{32}\) The other three samples showed peaks at 1.75 and 2.67 Å, which were similar to those of bulk CoO. As revealed by TEM, XRD, and EXAFS analyses, the CoO\(_x\) NPs in the CoO\(_x\)(4.3)/CNTs were mainly composed of the Co\(_3\)O\(_4\) phase, whereas the CoO\(_x\) NPs in the other three samples consisted of the CoO phase.

The structural changes of the CoO\(_x\) NPs under OER and ORR conditions were scrutinized using in situ electrochemical XAS with a homemade spectroelectrochemical cell. Figure 3a depicts in situ Co K-edge X-ray absorption near-edge spectroscopy (XANES) spectra of the CoO\(_x\)/CNTs measured at open circuit potential (OCP) and ORR potential (1.8 V vs reversible hydrogen electrode, RHE) in 0.1 M KOH electrolyte. Under the OER potential, the XANES spectra of Figure 3a) and in situ XANES spectra at the OCV (long dashed curves in Figure 3b) were negatively shifted, which indicated the diminishment of Co\(_3\)O\(_4\) characteristic peaks as well as the evolution of CoOOH-like peaks. From these observations, we concluded that the surfaces of the CoO\(_x\) NPs may be covered with a few layers of CoOOH because CoOOH is a thermodynamically stable phase under oxidizing potentials.\(^{36–38}\) We noted that the oxidation of the CoO\(_x\) NPs occurred even at the OCV, as revealed by distinct changes between ex situ XANES spectra (solid curves in Figure 3a) and in situ XANES spectra at the OCV (long dashed curves in Figure 3a). We attributed it to the intermediate range of OCV (0.9–1.1 V vs RHE), which is between ORR and OER potentials. This phase transformation under nonelectrocatalytic conditions is beyond the scope of this work and is subject to detailed investigation.

When the XANES spectra were measured under the ORR potential (0.6 V vs RHE), all the CoO\(_x\)/CNTs samples exhibited CoO\(_x\)/CoOOH-like XANES spectra, similar to the results of the XANES spectra taken under the OER potential, indicating the evolution of the Co(III) species during the ORR (Figure 4a). To access more detailed information, we scrutinized the XANES data with LCF analyses. The LCF analysis of in situ XANES at 0.6 V revealed that the CoO\(_x\) NPs exist in Co\(_3\)O\(_4\) and CoOOH phases with a small amount of Co\(_3\)O\(_4\)/CoOOH-like XANES spectra, similar to the CoO\(_x\)(9.5)/CNTs after the OER (Figure 3c).

The structural transformation was further observed by in situ EXAFS spectra of the CoO\(_x\)(4.3)/CNTs (Figure 3b). The RDF curve under OER potential compared to that under OCV revealed three major changes. First, a slight shrinkage in Co–O bond length was observed under the OER potential for CoO\(_x\)(4.3)/CNTs when compared to that under OCV (inset of Figure 3b). This is an indication of an increase in the oxidation state,\(^{32}\) possibly from CoO\(_x\) to CoOOH. Second, the RDF peak intensities for Co–O and Co–Co increased, which correspond to the increase in the amount of adjacent di-\(\mu\)-oxo-bridged CoO\(_x\) octahedra composing CoOOH\(^{33}\) that have been identified as an active phase for OER.\(^{34,35}\) Finally, under OER potential, the intensity of third major RDF peak intensity at 3.04 Å decreased, and the fourth major peak at 4.69 Å was negatively shifted, which indicates the diminishment of Co\(_3\)O\(_4\) characteristic peaks as well as the evolution of CoOOH-like peaks. From these observations, we concluded that the surfaces of the CoO\(_x\) NPs may be covered with a few layers of CoOOH because CoOOH is a thermodynamically stable phase under oxidizing potentials.\(^{36–38}\) We noted that the oxidation of the CoO\(_x\) NPs occurred even at the OCV, as revealed by distinct changes between ex situ XANES spectra (solid curves in Figure 3a) and in situ XANES spectra at the OCV (long dashed curves in Figure 3a). We attributed it to the intermediate range of OCV (0.9–1.1 V vs RHE), which is between ORR and OER potentials. This phase transformation under nonelectrocatalytic conditions is beyond the scope of this work and is subject to detailed investigation.
Co(OH)$_2$ in all samples (Table 1). The detailed numerical analysis revealed that with increased CoO$_x$ size the portion of Co$_3$O$_4$ increased whereas that of CoOOH decreased. The comparison of average oxidation state indicated a slightly lower oxidation state of the CoO$_2$(9.5)/CNTs than that of the other CoO$_x$/CNTs samples, perhaps because of a low surface fraction of the CoO$_2$ NPs that can participate in phase transformation (Table 1).

The above XANES results under ORR potential could be further substantiated by in situ EXAFS results, which also identified Co$_3$O$_4$ and CoOOH phases as major species (Figure 4b). In the RDFs of the in situ EXAFS spectra at 0.6 V, the first two peaks, corresponding to Co−O and Co−Co interatomic distances appeared for all of the CoO$_x$/CNTs. The other peaks at around 3.1 and 4.5 Å were also observed, which are known to originate from the Co$_3$O$_4$ and CoOOH phases (indicated by dashed lines in Figure 4b). The similar peak intensities between the samples except for the CoO$_2$(9.5)/CNTs indicated that they had almost identical local structure. The different structural properties of the CoO$_2$(9.5)/CNTs could be attributed to a lower portion of CoOOH and larger amount of Co$_3$O$_4$ comprising the CoO$_2$(9.5)/CNTs than those of the other samples, as evidenced by LCF analysis (Table 1).

When the applied potential was changed from OCV to ORR potential (0.6 V), the average oxidation state increased from ~ +2.5 to ~ +2.8, as revealed by the LCF analyses (Table 1 and Figure S3). The LCF analysis results indicated that Co(II) and Co(III) species were present in a ratio of around 1:1 at OCV, and Co(III) became the major species under the ORR potential. Some previous works consistently suggested that Co(II) on CoO$_x$ is relevant to catalytically active species for the ORR. In another early work, theoretical calculations suggested that the ORR on CoOOH is initiated over the Co(II) site followed by oxidation of the Co(II) to Co(III) species, which return to the Co(II) species for the next catalytic turnover. However, our in situ XAS result could not confirmatively conclude that the Co(III) species evolved at 0.6 V represents the catalytic intermediate in the ORR. As discussed in the electrochemical analysis below, in the CoO$_x$/CNTs, O$_2$ is initially reduced to peroxide catalyzed predominantly by the CNTs and subsequently the CoO$_2$ NPs disproportionate to the peroxide. The peroxide intermediate likely oxidizes the initial Co(II) species to Co(III) species concomitant to the peroxide disproportionation.

Next, the redox behavior of the samples was assessed via cyclic voltammetry (CV) in N$_2$-saturated 1 M KOH (Figure 5 and Figure S5). The CV results showed anodic peaks I, II, and III, which could be attributed to the oxidation of Co(II) to Co(III), the phase transition from Co$_3$O$_4$ to CoOOH, and the oxidation of Co(III) to Co(IV), respectively. The consecutive CV curves of the CoO$_x$/CNTs, compiled from up to 5 sequential scans, revealed the gradual decrease of anodic peak II and nearly constant peak III, indicating an irreversible transition of surface Co$_3$O$_4$ to CoOOH and the reversible transition of Co(III) to Co(IV), respectively. Frei and co-workers reported that Co(III) species act as an initiator for the OER process. Stahl and co-workers suggested that the key process in the OER is related to the reversible interconversion between Co(III) and Co(IV). The reversible redox transition between Co(III) and Co(IV) in the CoO$_x$/CNTs-catalyzed OER was also observed by the presence of anodic peak III in consecutive CV scans (Figure S4), which is consistent with these previous works. Significantly, in the first

![Figure 5. Redox properties of CoO$_2$/CNTs. (a) First CV curves over a potential range of 0.05−1.5 V (vs RHE) at a scan rate of 20 mV s$^{-1}$ in N$_2$-saturated 1 M KOH. (b) An enlarged view around anodic peak II (indicated by the dotted box in a). (c) Potentials at the anodic peak II positions versus particle size.](Image 346x316 to 543x749)
XAS could not reflect the initial oxidation state of Co of fresh CoOx/CNTs. In contrast, under potentiodynamic conditions of the CV scans, the step-by-step transitions of oxidation states in CoOx NPs could be detected.

Electrocatalytic OER and ORR activities were measured using the rotating disk electrode (RDE) in 0.1 M KOH (Figure 6 and Table S2). In the series of CoOx/CNTs, the OER activities increased with decreasing NP size; the potentials required to reach a current density of 10 mA cm\(^{-2}\) were 1.62, 1.64, 1.65, and 1.68 V for the CoOx(4.3)/CNTs, CoOx(6.3)/CNTs, CoOx(7.5)/CNTs, and CoOx(9.5)/CNTs, respectively (Figure 6a). The greater OER activities in smaller CoOx NPs were likely attributed to the large active surface areas\(^27\) and the abundance of Co(III) that is the main source for the active Co(IV) species, as confirmed by the CV anodic peak (Figure 5).\(^36,44\) The Tafel slopes were 69, 69, 73, and 80 mV dec\(^{-1}\) for the CoOx(4.3)/CNTs, CoOx(6.3)/CNTs, CoOx(7.5)/CNTs, and CoOx(9.5)/CNTs, respectively (Figure 6b). A smaller Tafel slope was obtained for the smaller CoOx catalyst, indicating more favorable reaction kinetics. In CoOx-based OER catalysts, high oxidation state Co(IV) centers have been suggested to play an essential role in catalyzing the OER.\(^36,37,45,46\) Active Co(IV) species arise from the oxidation of Co(III) with oxidizing potential, as evidenced by the anodic peak III of the CVs (Figure S4).

Unlike the case of the OER conditions, the CoOx/CNTs demonstrated nearly identical activities for the ORR independent of the CoOx NP size (Figure 6c). The onset potentials and diffusion-limited currents of the CoOx/CNTs were almost the same regardless of the NP sizes. Interestingly, the onset potential of the CoOx/CNTs was the same as those of the CNTs, and the Tafel plots of the CoOx/CNTs and CNTs almost overlapped (Figure 6d). This result suggested that the CoOx NPs did not improve the intrinsic ORR activity; rather, CoOx appeared to promote the reduction or disproportionation of peroxide species generated by the CNTs, as evidenced by the greater diffusion-limited currents of the CoOx/CNTs compared to those of the CNTs. In addition, the similar Tafel slopes might have indicated that the reaction rates of the CoOx/CNTs and CNTs were limited by the same step, which occurred on the CNTs.

Therefore, we hypothesized that the ORR was initiated by the CNTs via the two-electron transfer pathway and that the CoOx NPs mainly played an auxiliary role, promoting the reduction or disproportionation of the generated peroxide. The fast and repetitive disproportionation of peroxide by CoOx led to the quasi-four-electron pathway for the ORR.\(^28,47\) We again confirmed the particle size independence of the ORR activity trend with CoOx/CNTs with a higher CoOx loading (Table S3 and Figure S5). The ORR activities of 32% CoOx(4.3)/CNTs, 35% CoOx(6.3)/CNTs, and 36% CoOx(9.5)/CNTs were almost the same regardless of their particle sizes, as evidenced by their overlapping LSV curves. It was also found that the high-loading 32% CoOx(4.3)/CNTs showed only marginal improvement of the ORR activity in the kinetic region (i.e., 0.7–0.85 V) compared with the low-loading 9.4% CoOx(4.3)/CNTs. We found that the previously reported, high-performance CoOx/carbon hybrid catalysts usually contained nitrogen,\(^16,23,30\) potentially creating Co–N moieties, which are known to be highly active species for the ORR. The rather low ORR performances of our CoOx/CNTs are rationalized by the absence of nitrogen. We highlight the importance of preparing N-free metal oxides/carbon hybrid model catalysts to
investigate the particle size-dependent ORR activity originating from only metal oxides.

Long-term stability is a critical factor for applying electrocatalysts in practical applications. Chronopotentiometry (CP) was conducted at a current density of 5 mA cm\(^{-2}\) (Figure S6). The CoO\(_x\)/CNTs catalysts exhibited excellent durability with little decay in the OER activity and maintenance of their structures over 400 min of operation. TEM images after the CP measurements revealed that the phase of the CoO\(_x\) NPs was maintained as CoO\(_x\) with retained particle sizes for the CoO\(_x\)(4.3)/CNTs (Figure S7b). However, a long-term test under an applied OER potential resulted in the structural change from CoO to CoO\(_x\) for the largest CoO\(_x\) NPs, as revealed by the FFT patterns in Figure S7d, which was consistent with the in situ XAS measurement results. In addition, we investigated the chemical states of Co before and after chronopotentiometry (CP) using X-ray photoelectron spectroscopy (XPS) (Figure S8). For the CoO\(_x\)(4.3)/CNTs, the XPS spectra before and after the CP runs almost overlapped. For the CoO\(_x\)(9.5)/CNTs, satellite peaks around 787 and 803 eV (indicated by dotted lines) disappear after OER, indicating a decrease in the number of surface Co(II) species via the oxidation of Co(II) species to Co(III). The results support well the conclusions drawn from the other characterizations, including TEM, XRD, XAS, and CV curves.

## CONCLUSIONS

In summary, we have investigated the size-dependent NP structures and catalytic activities of the CoO\(_x\)/CNTs for bifunctional oxygen electrocatalysis. In situ electrochemical XAS measurements demonstrated that CoO\(_x\) and CoOOH were the major species regardless of the CoO\(_x\) particle size under both OER and ORR conditions. The OER activities of the CoO\(_x\)/CNTs increased with decreasing particle size, which could be associated with the increased oxidation state and larger surface area of the smaller NPs. The ORR activity was independent of the CoO\(_x\) NP size, revealing the auxiliary role of CoO\(_x\) on the CoO\(_x\)/CNTs for the reduction or disproportionation of peroxide rather than the reduction of oxygen. Combining in situ XAS with electrocatalytic activity trends, we suggested that the dominant Co(III) species are related to active intermediates for the OER, whereas they appear to be side products generated from the oxidation of Co(II) by a peroxide intermediate during the ORR. This work can offer a platform to explore the structural changes and reaction pathways of cobalt oxide for the rational design of advanced bifunctional oxygen electrocatalysts.

## MATERIALS AND METHODS

**Synthesis of Size-Controlled Cobalt Oxide Nanoparticles.** Cobalt oxide nanoparticles were synthesized via a previously reported method\(^{26}\) with some modifications. For the synthesis, standard Schlenk techniques were used, and all manipulations with the cobalt carbonyl precursor were performed in a glovebox. First, 73 \(\mu\)L of oleic acid (99%, Sigma-Aldrich) in a 100 mL round-bottom flask were evacuated for 10 min and saturated with Ar. Subsequently, 7.5 mL of anhydrous \(\sigma\)-dichlorobenzene (DCB, 99%, Sigma-Aldrich) were added. The flask was equipped with a long Liebig condenser, gas-volume spacer, and gas-release line to accommodate the large volume of CO, which was produced upon decomposition of the carbonyl precursor. With vigorous stirring, the mixture was heated to one of the desired temperatures (164, 168, 176, or 182 °C) at a heating rate of 5 °C min\(^{-1}\) under an Ar atmosphere. Once stabilized at the desired temperature, 1.5 mL of Co\(_2\)(CO)\(_8\) (Sigma-Aldrich) in DCB (0.5 M) was quickly injected into the heated solution. The transparent, brownish solution immediately turned black, indicating the formation of colloidal nanoparticles. This colloidal suspension was aged for 20 min prior to stopping the heating and then cooled in a flow of air. For the cobalt nanoparticles to be separated, 5 mL of DCB and 25 mL of 2-propanol (99%, Sigma-Aldrich) were added to the suspension, followed by centrifugation at 8000 rpm for 15 min. After discarding the supernatant, precipitated nanoparticles were dispersed in chloroform (CHCl\(_3\), Samchun).

**Acid Treatment of the CNTs.** First, 2.5 g of carbon nanotubes (CNTs, Carbon Nanomaterial Technology Company, MR 99) were mixed with 380 g of 6 M HCl (Samchun), and the mixture was stirred at 80 °C for 12 h. The suspension was filtered, washed with copious amounts of deionized (DI) water until the pH of the filtrate reached 7, and dried at 60 °C. The HCl-treated CNTs were subsequently washed with 390 g of 6 M HNO\(_3\) (Samchun).

**Synthesis of the CoO\(_x\)/CNTs.** The CoO\(_x\) nanoparticles (NPs) loaded on the CNTs (CoO\(_x\)/CNTs) were synthesized as follows. First, 350 mg of CNTs were dispersed in 50 mL of CHCl\(_3\) in a 100 mL Erlenmeyer flask. The flask was covered with Parafilm to avoid evaporation of the CHCl\(_3\). After stirring for 15 min, 38.9 mg of the as-prepared cobalt nanoparticles, dispersed in CHCl\(_3\), were added dropwise to the solution. Subsequent sonication in ice water for 3 h led to the homogeneous dispersion of CoO\(_x\) nanoparticles on CNTs. The product was collected by centrifugation and dried at 60 °C. Finally, the surfactants surrounding the nanoparticles were removed following a previously reported method.\(^{48}\) The dried powder was annealed by raising the temperature from room temperature to 185 °C for 2 h and maintained at that temperature for 5 h under air. For comparative purposes, acid-treated CNTs without CoO\(_x\) were also annealed at 185 °C for 5 h in the same manner as above.

**Synthesis of CoOOH.** CoOOH was synthesized for use as a reference material for the X-ray absorption spectroscopy study, as previously reported.\(^{49}\) First, Co(OH)\(_2\) powder (Sigma-Aldrich) was dispersed in 40 mL of DI water. Next, 10 mL of 8 M NaOH was added dropwise, and 4 mL of H\(_2\)O\(_2\) (30%, Sigma-Aldrich) was subsequently added with vigorous stirring. This reaction produces an explosive amount of O\(_2\) gas. The resulting dark-brown-colored suspension was stirred at 45 °C for 28 h. The product was filtered, washed with DI water several times, and dried overnight at 60 °C. The resulting CoOOH was found to be phase-pure with large crystallite size as revealed by XRD (Figure S9).

**Characterization Methods.** Scanning electron microscopy (SEM) analysis was conducted on a Hitachi S-4800 scanning electron microscope operating at 10 kV. High-resolution transmission electron microscopy (HR-TEM) images were taken on a JEOL JEM-2100 electron microscope at an acceleration voltage of 200 kV. Atomic-resolution TEM (ARTEM) images were taken with a low-voltage spherical aberration-corrected TEM (FEI Titan\(^3\) G2 60–300 with an image Cs corrector) with an acceleration voltage of 80 kV. X-ray powder diffraction (XRD) patterns were obtained with a high power X-ray diffractometer (Rigaku) equipped with Cu K\(_\alpha\) radiation and operated at 40 kV and 200 mA. Wide-angle XRD patterns were measured in a 2\(\theta\) range from 10° to 80° at a...
X-ray Absorption Spectroscopy Experiments. X-ray absorption spectroscopy (XAS) experiments were conducted on the Beamlines 6D and 10C of the Pohang Accelerator Laboratory (PAL) in South Korea with a beam energy and current of 3 GeV and 300 mA, respectively. X-ray photon energy was monochromatized with a Si(111) double-crystal monochromator, which was detuned by around 15 and 30% at the 6D and 10C beamlines, respectively, to remove high-order harmonics. In situ XAS spectra were obtained by using a homemade spectroelectrochemical cell in fluorescence mode. Catalyst ink was dropped and dried on a piece of carbon fiber paper and contacted with the electrolyte (0.1 M KOH) in the cell. In situ XAS measurement at OCV was first conducted, and the subsequent XAS scan was then performed after applying ORR (0.6 V vs RHE, iR-corrected) or OER (1.8 V) potential for 1 h to give enough time for phase transformation. Background removal and normalization of the spectra were carried out by using IFEFFIT (Athena) software.

Electrochemical Measurements. Electrochemical characterization of the catalysts was performed using an IviumStat electrochemical analyzer at room temperature (25 °C) and atmospheric pressure using a three-electrode system. A graphite counter electrode and a Hg/HgO reference electrode were used. All potentials in this report were converted to the counter electrode and a Hg/HgO reference electrode were used. All potentials in this report were converted to the reversible hydrogen electrode (RHE) scale.

A rotating ring-disk electrode (RRDE) composed of a glassy carbon (GC) disk (4 mm in diameter) and a Pt ring was used. All potentials in this report were converted to the reversible hydrogen electrode (RHE) scale.

For the evaluation of the kinetics for the ORR, the kinetic current was extracted from the equation

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_i}$$

where $I$, $I_k$, and $I_i$ are the measured current, kinetic current, and exchange current density, respectively.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b00553.

Average particle sizes, OER and ORR activities, CO contents, TEM images and FFT patterns, SEM images, XANES and XPS spectra, CV and chronopotentiometry curves, and XRD patterns (PDF)

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#### Notes

The authors declare no competing financial interest.

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