Electronic Structure Engineering of LiCoO2 toward Enhanced Oxygen Electrocatalysis

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Abstract
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Keywords
oxygen, enhanced, electrocatalysis, toward, electronic, licoo2, engineering, structure

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Keywords: oxygen evolution reaction, oxygen reduction reaction, nanosheets, electronic structure, synergistic effect

Abstract:

Developing low-cost and efficient electrocatalysts for the oxygen evolution reaction and oxygen reduction reaction is of critical significance to the practical application of some emerging energy storage and conversion devices (e.g., metal-air batteries, water electrolyzers, and fuel cells). Lithium cobalt oxide is a promising nonprecious metal-based electrocatalyst for oxygen electrocatalysis; its activity, however, is still far from the requirements of practical applications. Here, a new LiCoO$_2$-based electrocatalyst with nanosheet morphology is developed by a combination of Mg doping and shear force-assisted exfoliation strategies towards enhanced oxygen reduction and evolution reaction kinetics. It is demonstrated that the coupling effect of Mg doping and the exfoliation can effectively modulate the electronic structure of LiCoO$_2$, in which Co$^{3+}$ can be partially oxidized to Co$^{4+}$ and the Co-O covalency can be enhanced, which is closely associated with the improvement of intrinsic activity. Meanwhile, the unique nanosheet morphology also helps to expose more active Co species.
This work offers new insights into deploying the electronic structure engineering strategy for the development of efficient and durable catalysts for energy applications.

1. Introduction

With increasing energy demands and depletion of fossil fuels, great concerns have been raised about the development and in particularly the substantial application of renewable energy. One potential strategy is to develop intelligent electrochemical conversion and storage systems that could efficiently utilize renewable sources of energy.\textsuperscript{1-4} The oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are kinetically sluggish, and therefore, significantly high overpotentials are required to drive the reactions.\textsuperscript{5-8} These reactions are usually the bottleneck for the energy efficiency of fuel cells, metal–air batteries, and water splitting.\textsuperscript{9-11} Developing active electrocatalysts is vital to achieve accelerated electrochemical reaction kinetics and to eventually obtain highly efficient electrochemical devices. Currently, precious metal-based materials, such as Pt, IrO\textsubscript{2}, and RuO\textsubscript{2}, are dominant among the catalysts for oxygen electrocatalysis because of their superior activity; although their large scale application is severely limited by their high cost and scarcity.\textsuperscript{12-17} Therefore, this necessitates the design and development of earth-abundant, stable, yet highly active electrocatalysts towards practical energy storage and conversion devices.

Transition metal oxides and their derivatives have been considered as promising electrocatalysts for the OER and ORR due to their earth-abundance and low cost, as well as intrinsic stability during the catalytic process.\textsuperscript{9, 18-24} Among the various metal oxides, lithium metal oxides with the formula Li\textsubscript{2}M\textsubscript{2}O\textsubscript{3} (where M is a transition metal), which have been widely applied as cathodes for lithium ion batteries, constitute a new class of electrocatalysts. It has been reported that superior catalytic activity could be achieved by pinning the transition metal redox energies at the top of the O-2p band.\textsuperscript{25-28} LiCoO\textsubscript{2} has recently been intensively explored as OER and ORR catalyst.\textsuperscript{27, 29-35} However, its catalytic activity still needs to be enhanced to meet the requirements of practical applications. Towards the intelligent design of high
performance electrocatalysts, two general strategies (enhancing the intrinsic activity and increasing the number of active sites) have been applied to improve the activity of targeted electrocatalysts.\textsuperscript{36} Creating defects, modulating the electronic structure, and tuning the lattice strain are significant strategies to enhance the intrinsic activity of catalysts.\textsuperscript{12-18} Nanostructure engineering by reducing the material’s dimension and size is the most commonly deployed approach to increase the exposure of active sites. In particular, two-dimensional (2D) materials possess exotic electronic properties and high surface atom ratio, which are significant for electrochemical reaction kinetics.\textsuperscript{37-38} Hence, engineering 2D-based nanostructures is attracting ever-increasing attention towards catalysis and energy storage applications.\textsuperscript{39-43} Moreover, the electronic conductivity of the catalyst system is also a vital factor for fast reaction kinetics.\textsuperscript{44} It should also be mentioned that nanostructure engineering can modulate the intrinsic activity of the catalyst as well under some circumstances.

Herein, a new LiCoO\textsubscript{2}-based electrocatalyst was designed and prepared by the coupling of Mg doping and shear force-assisted exfoliation strategies towards enhanced oxygen electrocatalysis kinetics. Substantially improved catalytic activity in both the ORR and OER and this could be attributed to the synergistic effects induced by doping with inert element Mg and exfoliation process, which caused favorable electronic structure variation of Co to achieve higher valence (Co\textsuperscript{4+}) and Co-O covalency, enhanced charge transfer ability, and abundant exposure of active sites. These findings demonstrate that structure engineering via several coupled strategies can provide new opportunities to provide the further development of cost-effective electrocatalysts with durable and high activity.

2. Results

2.1. Preparation of LiCo\textsubscript{0.95}Mg\textsubscript{0.05}O\textsubscript{2} (ELCMO) nanosheets and their crystal structure

In this work, LiCo\textsubscript{0.95}Mg\textsubscript{0.05}O\textsubscript{2} (LCMO) nanosheets were prepared through a solid-state reaction method followed by shear-assisted exfoliation, as schematically illustrated in Figure 1a. Bulk LiCo\textsubscript{0.95}Mg\textsubscript{0.05}O\textsubscript{2} powders were first synthesized by the solid-state reaction process,
then the bulk powders were exfoliated in ethanol to yield a colloidal solution that contained ELCMO nanosheets with lithium deficiency. (A detailed description of the synthesis process is included in the Experimental section.) Figure 1b shows the XRD patterns of LiCoO$_2$ (LCO), LCMO, exfoliated LCO (ELCO) and ELCMO. All the diffraction peaks can be indexed to the NaFeO$_2$-type structure with space group $R\bar{3}m$ (rhombohedral structure), and no extra diffraction peaks are observed. The (003) peak of LCMO slightly shifts to lower angles in contrast to LCO, demonstrating lattice expansion caused by the doping of Mg$^{2+}$ with a larger atomic radius. This can be verified by the calculated lattice parameters presented in Table S1 (Supporting Information). The intensity ratio of the (003) peak to the (104) peak ($I_{(003)}/I_{(104)}$) can be used to indicate the degree of crystal orientation.$^{[45]}$ As can be seen, the value of $I_{(003)}/I_{(104)}$ is increased substantially after exfoliation, signifying the crystal orientation of the (003) planes and the presence of lamellar structure (Figure 1c). The grain size

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**Figure 1.** (a) Schematic illustration of the preparation of ELCMO nanosheets. (b) XRD patterns of LCO, LCMO, ELCO and ELCMO catalysts. (c) The ratio of intensity of peak (003)/(104), and inset is the digital images of the solutions of exfoliated ELCO and ELCMO nanosheets dispersed in ethanol.
is reduced significantly after exfoliation, which can be confirmed by the increase of the full-
width-half maximum (FWHM) of the (003) diffraction peak.

Bulk powders of both LCO and LCMO have a typical layered structure (Figure S1 and
Figure S2, Supporting Information). The transmission electron microscopy (TEM) images
(Figure 2a and Figure S3a, Supporting Information) demonstrate that the LCMO and LCO
nanosheets were obtained successfully through the exfoliation process. Optical images of
colloidal solutions of ELCO and ELCMO nanosheets obtained through shear exfoliation are
presented in Figure 1c. The high-resolution TEM (HRTEM) image together with the selected
area electron diffraction (SAED) pattern of ELCMO (Figure 2b-c) indicate that high
crystallinity is sustained after exfoliation. Also, the SAED pattern is consistent with the
 corresponding reflections originating from layered LiCoO$_2$, suggesting that the exfoliated
nanosheets maintain the same hexagonal structure. The ELCO nanosheets also maintain the
same crystal structure, as shown in Figure S3b (Supporting Information). The aberration-
corrected high angular annular dark-field (HAADF) and annular bright field (ABF) scanning
transmission electron microscopy (STEM) images of ELCMO projected along the [\textit{\textbf{\text{\text{\text{1\text{1\text{1}}}]]}} space group, where Co ions locate at the octahedral sites and one Co ion is
surrounded by 6 Co ions. The HAADF-STEM and ABF-STEM images of LCMO are presented
in Figure S4 (Supporting Information), where the arrangement of Co is also revealed, and the
result is in good accordance with the schematic diagram of LiCoO$_2$ projected from [001]
direction. In order to better understanding the atomic surrounding environment of Co and Li
atoms, inverse fast Fourier transformation (IFFT) was conducted, as shown in Figure 2g. The
distribution of Li and Co ions are clearly observed and one Co ion is surrounded by 4 Li ions,
which is well consistent with the schematic crystal structure of LiCoO$_2$ viewed from the [\textit{\textbf{\text{\text{\text{1\text{1\text{1}}}]}]} direction (Figure 2i). The atomic arrangement can be observed more clearly from Figure 2h,
which is the corresponding colored image of Figure 2g. STEM mapping (Figure 2f) suggests that Co, Mg and O are homogeneously spatially distributed across the ELCMO nanosheets, illustrating that the element distribution is not affected by exfoliation.

Figure 2. Structural characterization of exfoliated ELCMO nanosheets. (a) TEM image. (b) HRTEM image. (c) SAED pattern viewed from the [001] direction. (d) HAADF-STEM image, with the inset showing the structure. (e) ABF-STEM image with the inset showing the corresponding FFT pattern. (f) STEM mapping for Co, Mg and O. (g) IFFT image of HAADF-STEM image. (H) Colored IFFT image of HADDF-STEM image. (i) Schematic illustration of ELCMO viewed from the [111] direction. Lithium atoms: green spheres; Cobalt atoms: blue spheres.

2.2. Electrocatalytic performance
The OER catalytic performance of ELCMO was first evaluated and compared with LCO, LCMO, and ELCO in 1 M KOH solution. As can be seen from the linear sweep voltammetry (LSV) curves in Figure 3a, the catalytic activity of LiCoO$_2$ is greatly enhanced after Mg doping or exfoliation, and ELCMO delivers the best catalytic activity by combining Mg doping and exfoliation strategies, also confirmed by CV curves (Figure S5, Supporting Information). Remarkably, ELCMO shows superior OER activity to IrO$_2$. The required overpotential decreases from 461 mV for LCO to 329 mV for ELCMO to a current density of 10 mA cm$^{-2}$. To acquire more insight into the OER activity, the turnover frequencies (TOFs) of those catalysts were further evaluated and compared, assuming that all Co ions are involved in the catalytic reaction. As demonstrated in Figure 3b and Table S2 (Supporting Information), the TOF of ELCMO reaches 0.3 s$^{-1}$ at an overpotential of 380 mV, which is significantly larger than that of LCO (0.0006 s$^{-1}$), LCMO (0.002 s$^{-1}$) and ELCO (0.02 s$^{-1}$). The electrochemical impedance spectroscopy results (Figure S6, Supporting Information) reveal that ELCMO exhibits substantially reduced reaction resistance (7 Ω) as compared to the other samples, which is also solid evidence for the fast electrochemical reaction kinetics. The Tafel slope of ELCMO (33.8 mV dec$^{-1}$) is greatly decreased as compared to LCMO (63.7 mV dec$^{-1}$) and ELCO (47.7 mV dec$^{-1}$), confirming the outstanding OER kinetics of ELCMO resulting from the synergistic effects of Mg doping and exfoliation (Figure 3c). The electrochemical active surface area (ECSA) of the samples were estimated based on the electrochemical double-layer capacitances ($C_{dl}$) determined from the cyclic voltammetry (CV) curves recorded in a non-Faraday region (Figure S7, Supporting Information). As indicated in Figure 3d, both Mg doping and the exfoliation process have a significant positive effect on the $C_{dl}$ value of the samples. As compared to bulk LCO, the $C_{dl}$ of ELCMO is enhanced near 42 times, signifying that much more active sites are present in ELCMO due to the synergistic effect of Mg doping and exfoliation strategies. It is worth noting that the variation of Tafel slope is not as significant as that of $C_{dl}$ and specific activity, because Tafel slope is the intrinsic property of material and it
has little relationship with the surface area and the number of the active sites. Moreover, as compared with IrO$_2$, ELCMO shows better durability performance during the chronoamperometry test (Figure S8, Supporting Information).

**Figure 3.** Electrocatalytic performance of LCO, LCMO, ELCO and ELCMO catalysts for the OER. (a) LSV curves in 1 M KOH solution at a scan rate of 5 mV s$^{-1}$. Inset is the overpotential required for $J=10$ mA cm$^{-2}$. (b) TOF calculated at an overpotential of 380 mV. (c) Tafel slope. (d) Current density differences plotted against scan rates.

The ORR activities of the LiCoO$_2$-based catalysts were evaluated as well. The CV results (Figure S9, Supporting Information) suggest that ELCMO exhibits much more positive oxygen reduction peak potential (0.686 V versus RHE) compared to LCO, demonstrating the enhanced ORR activity of ELCMO. **Figure 4a** presents the rotating-disk electrode voltammograms of ELCMO catalyst at different rotation rates at a sweep rate of 5 mV s$^{-1}$. And the corresponding profiles of LCO, LCMO and ELCO are presented in Figure S10, Figure S11 and Figure S12 (Supporting Information), respectively. ELCMO shows the best intrinsic activity among all the catalysts, and exhibits the highest half-wave potential of 0.679 V, as shown in Figure 4c and
Table S3 (Supporting Information). The electron transfer number (n) of ELCMO determined from the Koutecky–Levich plots is close to 4 (Figure 4b), indicating that ELCMO favors a 4e oxygen reduction process and first-order reaction kinetics. In addition, the excellent reaction kinetics of ELCMO can be confirmed by the reduced Tafel slope and decreased reaction resistance (Figure 4d and Figure S13, Supporting Information). ELCMO shows promising ORR stability as well, as verified by the chronoamperometry test (Figure 4e).

**Discussion**

The excellent electrocatalytic performances of ELCMO nanosheets towards oxygen evolution and reduction reactions may be attributed to three principal factors: enhanced electrical conductivity, increased number of active sites, and in particular modulated electronic configuration of Co.

Enhanced electrical conductivity could be an important contributor to the improved catalytic performance towards the oxygen electrocatalysis. On the one hand, Mg doping can increase the electrical conductivity of LCO because the concentration of the electronic holes is considerably enhanced and the Fermi level shifts into the valence band, resulting in excellent p-type conductivity.\(^{46-48}\) This is also well validated by the conductivity test results. The electrical conductivity of LCMO is determined to be 1.8×10\(^{-4}\) S cm\(^{-1}\) at room temperature, which is dramatically improved as compared to LCO (1.2×10\(^{-5}\) S cm\(^{-1}\)). On the other hand, thinning down the thickness of the bulk material to nanosheets is an effective way for improving electrical conductivity and it was reported that the density of electronic states around the Fermi level can be increased dramatically when bulk materials are transformed to nanosheets.\(^{49-51}\) The electrical conductivity of ELCMO (1.3×10\(^{3}\) S cm\(^{-1}\)) and ELCO (1.5×10\(^{-4}\) S cm\(^{-1}\)) are also greatly increased over that of LCMO and LCO after exfoliation, respectively.
**Figure 4.** Electrocatalytic performance of LCO, LCMO, ELCO and ELCMO catalysts for the ORR. (a) Rotating-disk voltammograms of ELCMO in O₂-saturated 0.1 M KOH with a scan rate of 5 mV s⁻¹ at different rotation rates. (b) Koutecky–Levich plots of ELCMO at different voltages. (c) Have-wave potential plots. (d) Tafel slopes. (e) CA of ELCMO on the RDE (1600 rpm) measured at 0.6 V (vs. RHE) in O₂-saturated 0.1 M KOH.

Moreover, an increased number of active sites also contribute to the higher catalytic activity of exfoliated samples. Mechanical shear exfoliation not only reduces the thickness of the bulk materials to nanosheets, but also decreases the later size of the nanosheets, as verified by Brunauer-Emmett-Teller (BET) measurements, the TEM and SEM images. The N₂
adsorption/desorption isotherm plot is presented in the Figure S14 (Supporting Information) and the results illustrate that the exfoliated ELCO and ELCMO nanosheets have the similar specific surface area, which are 32.7 and 32.9 m$^2$ g$^{-1}$, respectively, much larger than the bulk LCO (0.8 m$^2$ g$^{-1}$) and LCMO (1.7 m$^2$ g$^{-1}$). This confirms that the exfoliation strategy is an effective way to improve the specific surface area of LCO and the density of electrocatalytic active sites.

It is generally accepted that the electronic structure of transition metal (M) and M-O covalency have a close correlation with the oxygen electrocatalysis kinetics.\textsuperscript{[21-22]} Higher valence of the transition metal and enhanced M-O covalency could promote electron transfer between surface transition metal cations and the adsorbed reaction intermediates.\textsuperscript{[1,45]} Therefore, we applied X-ray photoelectron spectroscopy (XPS) to determine the electronic structure of surface Co and O ions. After incorporating Mg ions and exfoliation, the main peak of Co 2p$^{3/2}$ gets broadened and shifts toward higher binding energy together with the reduced intensity of the satellite peak area (Figure 5a). The FWHM of the Co 2p$^{3/2}$ peak increases from 3.6 to 3.74 eV and the relative satellite peak area decreases from 2.54 to 2.24 upon Mg doping (Table S4, Supporting Information). Similar phenomenon can be observed after mechanical shear exfoliation, which may be related to partial Li extraction during exfoliation, resulting in the transformation of spin ordering and charge ordering of Co ions. Combining the binding energy with the relative satellite peak area is a more effective way to evaluate the valence of Co than only using binding energy because the peak position is closely associated with the substance.\textsuperscript{[52]} The reduced satellite peak area and positive shift of the binding energy indicate that the valence of Co ions is increased after Mg doping and exfoliation. Furthermore, the oxidation process of Co$^{3+}$ can be confirmed by the positive shift of the Co 3p core peaks and Co 3s spectrum of the samples (Figure S15 and Figure S16, Supporting Information). Moreover, a partial oxidation process of O$^{2-}$ ions can be indicated by the variations of O1s XPS spectra, where the O1s peak, lattice oxygen peak (located at lower binding energy about 529 eV) and active oxygen peak on
the surface (higher binding energy) become broader toward higher energy region after doping and exfoliation treatment.\textsuperscript{32, 53-54} This confirms that both cobalt and oxygen undergo oxidation-type changes in their electronic structure, implying enhanced Co-O covalency and hybridization of metal 3d orbitals and O 2p states upon Mg incorporation and exfoliation strategies.

Electron energy-loss spectrometry (EELS) of Co (Figure 5c) also unravel the partial oxidation of Co\textsuperscript{3+}, where the ratio of L\textsubscript{2}/L\textsubscript{3} for LCMO increases by 8\% after exfoliation, confirming that the Co valence state can be improved through shear exfoliation.\textsuperscript{55} The Raman spectra reveal that the peak wavenumber for the A\textsubscript{1g} (597 cm\textsuperscript{-1}) and E\textsubscript{g} (487 cm\textsuperscript{-1}) bands of the LCMO, ELCO and ELCMO catalysts (Figure 5d) shift downwards as compared with LCO, which can be ascribed to the expansion of the c axis due to Mg doping and Li deficiency, corroborating the modification of the spin ordering of Co ions.\textsuperscript{56-57} The Co-L edge X-ray absorption near edge structure (XANES) spectra (Figure 6a) show that the Co-L edge of LCMO, ELCO and ELCMO becomes broadened and shift toward higher energy position, indicating the increment of Co-O bond covalency and the increased effective charge of the Co ions.\textsuperscript{58} This is also confirmed by the variation of O K-edge XANES spectra, where
Figure 5. (a) Co 2p XPS core spectra. (b) O 1s XPS core spectra. (c) EELS spectra of Co L₂,₃ edge. (d) Raman spectra of the samples.

A decrease in the A1 peak (unoccupied O 2p–Co 3d hybridized state located at 531.6 eV) intensity was revealed, signifying higher oxidation of the oxygen and increased Co-O covalency (Figure S17, Supporting Information). This may result from the rehybridization between Co and O atoms under the local structural distortion of CoO₆ octahedra induced by the synergistic effects of Li deficiency and Mg doping. In all, the results of the above analysis could be illustrated by the modification of qualitative one-electron energy diagram of Co³⁺ to Co⁴⁺ (Figure 6b). The formation of Co⁴⁺: 3d⁵ (t²₂g e⁰₉) due to the oxidation of low-spin Co³⁺ 3d⁶ (t⁶₂g e⁰₉) ions favors the reduction of the crystal field stabilization energy (CFSE), facilitating fast oxygen electrode reactions.⁹ In addition, the covalency and hybridization of metal 3d and O 2p states are improved significantly, accompanied by an increased hole concentration, resulting in enhanced charge transfer between surface Co cations and the adsorbates such as O₂⁻ and O²⁻, as illustrated in the Figure 6c. This is verified by the tendency for the Valence spectra of doped and exfoliated samples to exhibit a reduction of the peak Co 3d state (t₂g), particularly for ELCMO catalysts, which can be assigned to the reduction of the electron
population of the Co 3d states, resulting from the creation of holes in the t$_{2g}$ band created by overlapping t$_{2g}$ orbitals of Co in edge-sharing octahedral (Figure S18, Supporting Information).

Figure 6. (a) Normalized Co L-edge X-ray absorption spectra of the samples. (b) Qualitative one-electron energy diagram, illustrating the modulated electronic structure of Co and O. (c) Proposed OER and ORR mechanisms.

4. Conclusion

In summary, highly efficient LiCoO$_2$-based nanosheets were successfully prepared by combining Mg doping and exfoliation strategies towards enhanced oxygen electrocatalysis (OER and ORR). The combination of Mg doping and the exfoliation process could modulate the electronic structure of Co and the covalency of Co-O, and maximize the exposure of active sites, which eventually induce substantially enhanced electrocatalytic performance in terms of specific activity and stability. The present results provide new insights into the design and development of highly active catalysts for oxygen electrocatalysis towards energy applications (e.g., water electrolyzers, metal-air batteries).
Experimental Section

Synthesis of bulk LCO powders: Bulk LCO powders were prepared by a typical solid-state reaction from stoichiometric amount of Co$_3$O$_4$ (Sigma-Aldrich, 99.5%) and 4% excess Li$_2$CO$_3$ (Sigma-Aldrich, 99%). The precursors were dispersed into ethanol and then ground by ball milling for 8 h at a speed of 300 rpm. The slurry was dried in an oven at 80 °C for 8 h, followed by calcination at 480 °C for 2 h and then 950 °C for 4 h in air. The obtained LCO powders were stored in a glove box filled with Ar before use.

Synthesis of bulk LCMO powders: The synthesis procedure of bulk LCMO powders was the same as that of LCO, except that stoichiometric amount of Co$_3$O$_4$, MgO (Sigma-Aldrich, 99%) and 4% excess Li$_2$CO$_3$ were used.

Synthesis of ELCO and ELCMO nanosheets: ELCO and ELCMO nanosheets were prepared from the corresponding bulk LCO and LCMO via the shear-assisted exfoliation. In a typical procedure, 3 g of bulk LCMO powders were dispersed in 150 ml ethanol and the suspension was sonicated for 0.5 h. The as-prepared suspension was then exfoliated using a high shear laboratory mixer (L5M) with a rotor (30 mm in diameter) at 5500 rpm for 40 min. The resultant suspension was centrifuged at 2500 rpm for 30 min to remove the unexfoliated bulk material. The obtained supernatant was further centrifuged at 10000 rpm for 20 min to obtain the final LCMO nanosheets.

Structural Characterization: X-ray diffraction (XRD) was carried out on a GBC MMA diffractometer with Cu Kα1 radiation ($\lambda = 1.541$ Å, step size of 0.02°s$^{-1}$). The data were collected in the 2θ range of 10°-70°. The elemental and chemical composition of all the samples were determined by X-ray photoelectron spectroscopy (XPS, VG Multilab 2000). Raman spectroscopy was acquired on a JY HR800 spectrometer equipped with a 633 nm laser as the excitation source. The Brunauer–Emmett–Teller (BET) method was used to determine the specific surface area of the samples based on the nitrogen adsorption/desorption isotherms (Micromeritics, TriStarII). For conductivity measurements, the powders were pressed into
pellets and then silver paste was coated on the both sides of each pellet for current collecting. The resistance of the pellets was measured using a Keithley 196 System DMM at room temperature. The X-ray absorption near-edge spectra of Co and O were conducted at Beamline BL12b of the National Synchrotron Radiation Laboratory (NSRL, China). The morphologies of the catalysts were characterized by field-emission scanning electron microscopy (FESEM, JEOL JSM-7500) and transmission electron microscopy (TEM, JEM-2010). Annular bright field (ABF), high-angle annular dark field (HAADF) images and EELS were conducted on a 200 kV ARM-200F transmission electron microscope (JEOL) with a double aberration corrector and a cold field-emission gun.

Electrochemical characterizations: For the preparation of catalyst inks, 4 mg catalyst powders were dispersed in a mixed solution (16 µL of 5% Nafion solution, 384 µL of deionized water, and 100 µL of isopropanol) by sonicating for 2 h to obtain a homogeneous ink. For ORR activity evaluation, extra 1 mg of VulcanXC-72 was added as the conductive additive for all the catalysts. 10 µL of the catalyst ink was coated on a polished glassy carbon electrode (0.196 cm²) and dried in ambient air for OER activity evaluation, while 20 µL of the catalyst ink was applied for ORR activity evaluation. Electrochemical experiments were performed with a WaveDriver 20 potentiostat (Pine Research Instruments, US). All the measurements were carried out in KOH aqueous solution (0.1 M KOH for ORR and 1 M KOH for OER). A Hg/HgO electrode and a platinum net were applied as the reference electrode and counter electrode, respectively. Linear sweep voltammetry (LSV) was conducted at 5 mV s⁻¹ from 1.13 -1.83 V (versus RHE) at 1600 rpm for OER. While for the ORR measurements, the LSV was performed in oxygen saturated electrolyte at rotation speeds of 400, 625, 900, 1225, 1600 and 2025 rpm with the voltage range of 0.2-1.0 V versus RHE. The durability of the catalysts was determined by the chronoamperometry method, which was executed at 1.56 V (versus RHE) at a rotation speed of 1600 rpm for 2 h for the OER and 0.6 V (versus RHE) for 2 h for the ORR. The electrochemically active surface area (ECSA) was evaluated based on the double-layer
capacitance ($C_{dl}$) of the electrode. Electrochemical impedance spectroscopy (EIS) was performed in the frequency range of 100 kHz - 0.1 Hz. All the LSV results were IR corrected by subtracting the ohmic resistance loss.

**Supporting Information**

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

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**Conflict of Interest**

The authors declare no conflict of interest.

References


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**Keywords:** oxygen evolution reaction, oxygen reduction reaction, nanosheets, electronic structure, synergistic effect

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**TOC figure**