

# Engineering Local and Global Structures of Single Co Atoms for a Superior Oxygen Reduction Reaction

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efficient single-atom electrocatalysts (SAECs) that can surmount both thermodynamic and kinetic constraints in electrocatalysis. Here, we designed a core–shellstructured SAEC (Co<sub>1</sub>-SAC) with superior oxygen reduction reaction (ORR) performance. Co<sub>1</sub>-SAC consists of a locally engineered single Co-N<sub>3</sub>C<sub>1</sub> site on a Ndoped microporous amorphous carbon support enveloped by a globally engineered highly conductive mesoporous graphitic carbon shell. Theoretical calculations reveal that Co-N<sub>3</sub>C<sub>1</sub> exhibits near-Fermi electronic states distinct from those of Co-N<sub>2</sub>C<sub>2</sub> and Co-N<sub>4</sub>, which facilitate both the electronic hybridization with O<sub>2</sub> and the subsequent protonation of adsorbed O<sub>2</sub>\* toward the formation of OOH\*. Engineering Co-N<sub>3</sub>C<sub>1</sub>-SAC into a micro/mesoporous core–shell structure dramatically enhances the mass transport and electron transfer, which further boosts



the ORR and Zn-air battery performance (slightly outperforming Pt/C). Our findings open an avenue toward engineering of the local and global environment of SACs for a wide range of efficient electrochemical conversions.

KEYWORDS: single-atom catalysis, electrocatalysis, atomic structure engineering, accelerated kinetics, oxygen reduction reaction

## INTRODUCTION

Carbon-supported single-atom catalysts (SACs) have sparked an intensive interest in the field of electrocatalysis due to their maximized atom-utilization efficiency and outstanding performance in key electrocatalytic conversions.<sup>1-15</sup> For singleatom electrocatalysts to be practicably applicable, an abundance of highly active single-metal centers with rationally designed local coordination configuration embedded in porous and conductive support is greatly desired.<sup>16,17</sup> Hence, an ideal route toward the design of highly efficient single-atom electrocatalysts (SAECs) is to optimize both the local metal coordination environment and the global porosity and conductivity of the carbon support as well as the density of desired active sites.<sup>18</sup> This form of optimization not only reduces the thermodynamic potential barriers but also improves the sluggish reaction kinetics including mass transport and electron transfer and is thus of paramount importance in achieving superior electrocatalytic performances. Unfortunately, immobilization of a high loading of isolated metal atoms on the carbon support generally involves the introduction of numerous defective sites or doped heteroatoms, which in turn disrupts the delocalized  $\pi$ -bonded network in graphitic carbon domains and leads to a decrease in the overall electrical conductivity of the carbon matrix.<sup>19-22</sup> Despite tremendous progress in this field, controllable

synthesis of a high density of the desired single-metal sites on the carbon support with sufficiently high electrical conductivity and porosity remains a formidable challenge.

To this end, we design a synthetic route that involves controllable thermal pyrolysis of core-shell-structured zeolitic imidazolate frameworks (ZIFs), allowing for the fabrication of highly efficient core-shell SACs with rational control over their metal loading, local coordination environment, and global morphology. SAC synthesized here consists of a high density of locally optimized active sites (Co-N<sub>3</sub>C<sub>1</sub>) in N-doped microporous amorphous carbon (N-MAC) wrapped by a mesoporous conductive graphitic carbon (GC) shell. Both experimental and theoretical results reveal that the oxygen reduction reaction (ORR) proceeding over the Co-N<sub>3</sub>C<sub>1</sub> site is more energetically favorable compared to Co-N<sub>2</sub>C<sub>2</sub> and Co-N<sub>4</sub>.

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The outer mesoporous graphitic shell facilitates both mass transport and electron transfer, which dramatically enhance the ORR performance, making the SAC superior to the vast majority of non-noble SACs. Such a core-shell design of SAECs could surmount both thermodynamic and kinetic constraints for a broad range of superior electrochemical energy conversions beyond ORR.

#### EXPERIMENTAL SECTION

**Synthesis of Co/Zn-ZIF.** For the synthesis of Co/Zn-ZIF, both  $Co(NO_3)_2 \cdot 6H_2O$  (16.38 g) and  $Zn(NO_3)_2 \cdot 6H_2O$  (16.74 g) were dissolved in 300 mL of methanol to form a solution. Subsequently, the as-prepared solution is poured into 300 mL of methanol containing 18.36 g of 2-methylimidazole (MeIm) followed by stirring at room temperature for 12 h. The asobtained precipitates were centrifuged, washed several times with methanol, and dried at 80 °C overnight.

**Synthesis of ZIF-67.** For the synthesis of ZIF-67,  $Co(NO_3)_2 \cdot 6H_2O$  (10.92 g) and MeIm (12.32g) were dissolved in 200 mL of methanol separately to form two solutions. The MeIm solution was subsequently mixed with the solution  $Co(NO_3)_2 \cdot 6H_2O$ , followed by stirring at room temperature for 12 h. The as-obtained precipitates were centrifuged, washed several times with methanol, and dried at 80 °C overnight.

Synthesis of Heterostructured Co/Zn-ZIF@ZIF-67. For the synthesis of Co/Zn-ZIF@ZIF-67, Co/Zn-ZIF seeds (1200 mg) were first dispersed in 100 mL of methanol under sonication for 30 min to form a mixture solution.  $Co(NO_3)_2$ .  $6H_2O$  (3.06 g) and MeIm (3.45 g) were dissolved in 100 mL of methanol to form two solutions, respectively. Then, the solution of  $Co(NO_3)_2$ . $6H_2O$  was subsequently poured into the mixture solution of Co/Zn-ZIF, and the solution of MeIm was further poured into the above mixture solution. After the solutions were mixed and stirred at room temperature for 12 h, the as-obtained precipitates were centrifuged, washed several times with methanol, and dried at 80 °C overnight.

Synthesis of Co-N<sub>2</sub>C<sub>2</sub>, Co-N<sub>3</sub>C<sub>1</sub>, and Co-N<sub>4</sub>. The powder of Co/Zn-ZIF was placed in a tube furnace, heated up to the desired temperature (800 °C for Co-N<sub>4</sub>, 900 °C for Co-N<sub>3</sub>C<sub>1</sub>, and 1000 °C for Co-N<sub>2</sub>C<sub>2</sub>) with a ramp rate of 5 °C·min<sup>-1</sup>, kept for 12 h in a flow of argon, and then naturally cooled to room temperature.

**Synthesis of GC and Co-N<sub>3</sub>C<sub>1</sub>@GC.** The powder of ZIF-67 and Co/Zn-ZIF@ZIF-67 was placed in a tube furnace, heated up to 900 °C with a ramp rate of 5 °C·min<sup>-1</sup>, kept for 12 h in a flow of argon, and then naturally cooled to room temperature. The obtained black powders were washed thoroughly in 1 M  $H_2SO_4$  solution to remove any accessible Co particles.

**Material Characterization.** Wide-angle X-ray diffraction (XRD) patterns were collected on a Bruker D8 Focus Powder X-ray diffractometer using Cu K $\alpha$  radiation (40 kV, 40 mA) at room temperature. Scanning electron microscopy (SEM) images were taken on a JEOL JSM-6701F field emission microscope. Transmission electron microscopy (TEM) images were obtained with an FEI Titan 80-300 S/TEM working at 200 kV. Scanning transmission electron microscope-annular dark-field (STEM-ADF) imaging was carried out in an aberration-corrected JEOL ARM-200F system equipped with a cold field emission gun and an ASCOR probe corrector at 60 kV. The images were collected with a half-angle range from ~80 to 280 mrad, and the convergence semiangle was set at

~30 mrad. X-ray photoelectron spectroscopy (XPS) measurements were carried out in a custom-designed ultrahigh-vacuum system with a base pressure lower than  $2 \times 10^{-10}$  mbar. Al K $\alpha$  $(h\nu = 1486.7 \text{ eV})$  was used as the excitation source for XPS. The Co loadings in all of the samples were measured by an inductively coupled plasma atomic emission spectrometer; therein, all samples were dissolved in hot, fresh aqua regia. Raman spectroscopic measurements were performed on WITec Alpha 300R at room temperature with laser excitation at 532 nm. N<sub>2</sub> adsorption-desorption experiments were carried out at 77 K on Quantachrome Instruments AutosorbiQ (Boynton Beach, FL). The X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) measurements of Co K-edge were carried out at the XAFCA beamline of the Singapore Synchrotron Light Source (SSLS). The storage ring of SSLS was operated at 700 MeV with a beam current of 200 mA. A Si(111) doublecrystal monochromator was used to filter the X-ray beam. Co foils were used for the energy calibration, and all samples were measured under transmission mode at room temperature. The EXAFS oscillations  $\chi(k)$  were extracted and analyzed using the Demeter software package.

Electrochemical Tests. All of the measurements were carried out using a CHI 760E electrochemical workstation with a standard three-electrode setup. The electrocatalyst was prepared by mixing 4 mg of the catalyst powder, 1 mL of ethanol, and 20  $\mu$ L of 5 wt % Nafion solution followed by sonicating the mixture for 1 h. Then, 20  $\mu$ L of the catalyst suspension was drop-cast onto a freshly polished glassy carbon electrode (5 mm in diameter), leading to a loading density of 0.4 mg·cm<sup>-2</sup>. A glassy carbon electrode was used as the support for the working electrode. The Hg/Hg<sub>2</sub>Cl<sub>2</sub> electrode in saturated KCl and graphite rod served as the reference electrode and counter electrode, respectively. Prior to the measurement, the electrolyte was saturated with  $N_2/O_2$  by the gas flow through the cell for 30 min. The electrochemical experiments were conducted in an O2-saturated 0.1 M KOH solution for ORR at room temperature. The rotating disk electrode (RDE) tests were performed at various rotating speeds ranging from 900 to 2500 rpm with a sweep rate of 10 mV·s<sup>-1</sup>. The cyclic voltammetry experiments were performed in  $N_2/O_2$ -saturated 0.1 M KOH electrolyte solutions with a scan rate of 20 mV·s<sup>-1</sup>. The electron transfer number (n) can be calculated using the Koutecky-Levich equation

$$\frac{1}{J} = \frac{1}{J_{\rm L}} + \frac{1}{J_{\rm K}} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_{\rm K}},$$
$$B = 0.62nFC_{\rm o}D_{\rm o}^{2/3}V^{-1/6}$$

where J is the measured current density,  $J_{\rm K}$  and  $J_{\rm L}$  are the kinetic and limiting current densities,  $\omega$  is the angular velocity of the disk, n is the electron transfer number, F is the Faraday constant (96 485 C·mol<sup>-1</sup>),  $C_0$  is the bulk concentration of O<sub>2</sub> ( $1.2 \times 10^{-6} \text{ mol} \cdot \text{cm}^{-3}$ ),  $D_0$  is the diffusion coefficient of O<sub>2</sub> in 0.1 M KOH ( $1.9 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ ), and V is the kinematic viscosity of the electrolyte ( $0.01 \text{ cm}^2 \cdot \text{s}^{-1}$ ). For rotating ring-disk electrode (RRDE) tests, a computer-controlled CHI 760E electrochemical workstation was employed, the disk electrode was scanned cathodically at a rate of 5 mV·s<sup>-1</sup>, and the ring electrode (RHE). The hydrogen peroxide yield ( $H_2O_2$ %) and the electron transfer number (n) can be determined by the following equations

# Scheme 1. Schematic Illustration of the Formation of Locally and Globally Engineered Structure of Co-N<sub>3</sub>C<sub>1</sub>@GC



Co-N<sub>3</sub>C<sub>1</sub>@GC



**Figure 1.** Aberration-corrected STEM-ADF images of the as-synthesized (a)  $Co-N_4$ , (b)  $Co-N_3C_1$ , and (c)  $Co-N_2C_2$ . (d) The corresponding EDS mapping of  $Co-N_3C_1$  reveals a uniform distribution of Co and N on the carbon support. The Co K-edge of (e) FT-EXAFS and (f) XANES of Co-N<sub>4</sub>, Co-N<sub>3</sub>C<sub>1</sub>, and Co-N<sub>2</sub>C<sub>2</sub>. (g) The corresponding EXAFS fitting curves for  $Co-N_3C_1$ . The inset shows the proposed structure.

$$H_2O_2(\%) = 200 \times \frac{I_R/N}{(I_R/N) + I_D}$$
$$n = 4 \times \frac{I_D}{(I_R/N) + I_D}$$

Here,  $I_D$  is the disk current,  $I_R$  is the ring current, and N = 0.4 is the current collection efficiency of the Pt ring.

**Density Functional Theory (DFT) Calculations.** The Co-N<sub>x</sub> (x = 2, 3, and 4) nanosheets are modeled based on single Co atom-doped double-vacancy 7 × 7 graphene. A certain number (x) of C atoms near the doped Co atom are replaced with N atoms, which makes the Co atom bonded with

two kinds of N atoms (pyrrolic and pyridinic). A vacuum layer of 15 Å is added to avoid the interaction with its mirror images. The first-principles calculations are performed with spin-polarized density functional theory (DFT) as implemented in in Vienna ab initio simulation package (VASP).<sup>23–25</sup> A plane wave basis with a cutoff energy of 450 eV is employed in all calculations with the generalized gradient approximation in the PBE format<sup>26</sup> and the projector-augmented wave method.<sup>27</sup> A  $2 \times 2 \times 1 k$  points sampling is applied in geometry and lattice optimization calculations. The convergence criteria for electronic steps and structural relaxations are set to  $10^{-5}$  eV and 0.01 eV·Å<sup>-1</sup>, respectively. The vibrational frequency



**Figure 2.** (a) Linear sweep voltammetry (LSV) curves of Co-N<sub>4</sub>, Co-N<sub>3</sub>C<sub>1</sub>, and Co-N<sub>2</sub>C<sub>2</sub> in an O<sub>2</sub>-saturated 0.1 M KOH solution at a sweep rate of 10 mV·S<sup>-1</sup> and electrode rotation speed of 1600 rpm. (b) Mass activity for different catalysts. (c) Reaction energy diagram of Co-N<sub>4</sub>, Co-N<sub>3</sub>C<sub>1</sub>, and Co-N<sub>2</sub>C<sub>2</sub> at U = 0.462 V. (d) Calculated charge density distributions, and (e) projected density of states (PDOS) for the Co center, atoms in the first coordinate shell, and oxygen of Co-N<sub>4</sub>, Co-N<sub>3</sub>C<sub>1</sub>, and Co-N<sub>2</sub>C<sub>2</sub>, respectively. Fermi energy is set to zero.

calculations are carried out to obtain the zero-point energies of the species in ORR. The entropy values of the  $O_2$  molecule is adopted from the NIST database.<sup>28</sup>

# RESULTS AND DISCUSSION

The electronic and catalytic properties of the supported single atoms are highly susceptible to their local chemical environment.<sup>29-38</sup> We, therefore, attempted to tune the ratio between the proximal N and C atoms bonded to single cobalt atoms by controlling thermal pyrolysis of rationally designed ZIFs (Scheme 1). The cobalt metal nodes of ZIFs can be reduced and embedded in the N-doped carbon matrix at elevated temperatures, consistent with previous results.<sup>30</sup> It is also found that three types of single-Co-atom catalysts with different numbers of proximal N atoms (denoted Co-N<sub>4</sub>, Co- $N_3C_1$ , and  $Co-N_2C_2$ ) can be obtained by thermal pyrolysis at 800, 900, and 1000 °C, respectively. We then carried out STEM-ADF measurements of these samples to probe the dispersion of Co atoms in the carbon support. Atomicresolution STEM-ADF (Figures 1a-c and S1) images show that individual Co atoms are atomically dispersed on the microporous amorphous carbon support in these three samples. In addition, Co, C, and N atoms are distributed uniformly over the entire architecture, as evidenced by the energy-dispersive X-ray spectroscopy (EDS) mapping (Figure 1d). The local coordination environment of Co atoms in different samples was investigated using extended EXAFS spectroscopy (Figure 1e). The Fourier transforms (FT) of Co K-edge EXAFS spectra of all of the Co1-SAC samples exhibit a prominent peak at ca. 1.4 Å, attributed to the Co-N/C coordination bond. The absence of a Co-Co bond-related peak at a higher R value confirms that all of the Co species in these samples retain the atomic dispersion after thermal pyrolysis at high temperature up to 1000 °C. The spectra acquired over these SACs (Co-N<sub>4</sub>, Co-N<sub>3</sub>C<sub>1</sub>, and Co-N<sub>2</sub>C<sub>2</sub>) reveal that a decrease of the ratio of the nearest neighboring N/C atoms shifts the peak associated with Co-N(C) toward a smaller *R* value. This is because the Co–C bond is shorter than the Co-N bond.<sup>30</sup> Additionally, the simulated Co K-edge EXAFS (Figures 1g, and S2) spectra of the proposed atomic models (Co-N<sub>4</sub>, Co-N<sub>3</sub>C<sub>2</sub>, and Co-N<sub>2</sub>C<sub>2</sub>) show good agreement with the experimental results (Table S1), which is also consistent with previous studies.<sup>19</sup> XANES spectroscopy was used to probe the valence state of the Co species of these samples, as shown in Figure 1f. An increase of annealing temperature results in a noticeable shift of shoulder toward lower energy for the spectra acquired over these three SACs (800, 900, and 1000 °C), suggesting a reduction of the number of proximal N atoms bonded to the Co center as a function of pyrolysis temperature. This is because a decrease of the N/C ratio bonded to the Co center tends to decrease the oxidation state of the central Co atom due to a lower electronegativity of C compared to that of the N atom.

The ORR performance of this series of SACs (Co-N<sub>2</sub>C<sub>2</sub>, Co-N<sub>3</sub>C<sub>1</sub>, and Co-N<sub>4</sub>) was tested using the RDE with an O<sub>2</sub>-saturated 0.1 M KOH solution. As revealed by linear sweep voltammetry (LSV) results (Figure 2a), Co-N<sub>3</sub>C<sub>1</sub> shows the best ORR activity with a half-wave potential ( $E_{1/2}$ ) of 0.824 V (vs RHE) and an onset potential ( $E_{onset}$ ) of 0.904 V. In contrast, the half-wave potential and onset potential of Co-N<sub>4</sub> ( $E_{1/2} = 0.787$  mV,  $E_{onset} = 0.876$  mV) and Co-N<sub>2</sub>C<sub>2</sub> ( $E_{1/2} = 0.806$  mV,  $E_{onset} = 0.900$  mV) shift toward to a lower value by 37 (28) and 18 (4) mV, respectively (Table 1). The residual Zn species has a negligible effect on the improvement of the catalysts' ORR performance as the pure Zn-ZIF-derived Zn-

Table 1. Onset Potential, Half-Wave Potential, Mass Activity, and TOF of Co-N<sub>4</sub>, Co-N<sub>3</sub>C<sub>1</sub>, Co-N<sub>2</sub>C<sub>2</sub>, Co-N<sub>3</sub>C<sub>1</sub>@ GC, GC, and Pt/C Catalysts<sup>a</sup>

sample	onset potential (V)	half-wave potential (V)	mass activity at 0.8 V (A⋅mg <sub>metal</sub> <sup>-1</sup> )	TOF at 0.8 V (S <sup>-1</sup> )
Co-N <sub>4</sub>	0.876	0.787	0.52	0.34
$Co-N_3C_1$	0.904	0.824	0.77	0.46
$Co-N_2C_2$	0.900	0.806	0.56	0.28
Pt/C	0.943	0.847	0.12	0.45
Co-N <sub>3</sub> C <sub>1</sub> @GC	0.913	0.854	NA	NA
GC	0.868	0.810	NA	NA
<sup><i>a</i></sup> NA, not applicable				

nitrogen-doped carbon shows a very poor activity compared to Co-N<sub>3</sub>C<sub>1</sub> (Figure S3). Apart from the onset and half-wave potentials, Co-N<sub>3</sub>C<sub>1</sub> also shows the highest mass activity of 0.77 A  $mg_{Co}^{-1}$  at 0.8 V vs RHE (Figure 2b) (normalized by the total mass of loaded Co (Table S2)) and the highest turnover frequency (TOF) of 0.46 S<sup>-1</sup> (Table 1) among all of the SACs tested.

To understand the different catalytic properties of these systems, we first calculated the electronic structures of the  $CoN_r$  series using DFT. The atomic structure of these active sites with the corresponding charge density redistribution upon O<sub>2</sub> adsorption is shown in Figure 2d. Figure 2e presents the calculated projected density of states (PDOS) of the Co atom and the adjacent N and C atoms in different CoN<sub>x</sub> structures together with gas-phase like molecular O<sub>2</sub> orbital well above the  $CoN_r$  site (>4 Å, before adsorption). It is found that the ratio of N to C coordinated with the single Co site has a significant impact on the distribution of Co d states near-Fermi energy  $(E_{\rm F})$ . In contrast to Co-N<sub>2</sub>C<sub>2</sub> and Co-N<sub>4</sub>, there is a significant overlap between DOSs of Co d of Co-N<sub>3</sub>C<sub>1</sub> and the empty O<sub>2</sub>  $2\pi^*$  state right above  $E_{\rm F}$ , presumably resulting in a stronger hybridization between Co d of Co-N<sub>3</sub>C<sub>1</sub> and O<sub>2</sub>  $2\pi^*$ near  $E_{\rm F}$ . We then calculated the electronic structures of chemically adsorbed  $O_2$  molecules over different  $CoN_x$  (x = 2, 3, 4) under the most energetically favorable configuration.

Upon  $O_2$  adsorption, the  $O_2/Co-N_3C_1$  system shows broad electronic states spanning across  $E_{\rm F}$  resulting from a strong hybridization of Co d and the empty  $O_2 2\pi^*$  states. In contrast,  $O_2/Co-N_2C_2$  and  $O_2/Co-N_4$  show a gaplike feature close to  $E_F$ . It is expected that the presence of near-Fermi electronic structures of the  $O_2/Co-N_3C_1$  system could favor the electron transfer process for the subsequent protonation of adsorbed O<sub>2</sub>, one of the key steps in the ORR reaction (Figure S4, Table S3). We then calculated the free energies of each elementary step of ORR over different active sites. The calculated reaction free energy diagram with potential (U) corrections is shown in Figure 2c. U = 0.462 V is chosen for the calculated reaction free energy diagram of ORR to match the experimental conditions (the reaction happens at pH = 13), which determines the chemical potential of H. The protonation of adsorbed O2 is revealed to be the rate-determining step (Figure S5). Among all of the  $CoN_x$  structures tested, Co-N<sub>3</sub>C<sub>1</sub> is predicted to show the best electrocatalytic performance due to the lowest  $\Delta G_{\text{max}}$  for the rate-limiting step (0.052) eV) at U = 0.462, lower in energy by 0.09 and 0.22 eV compared to Co-N<sub>2</sub>C<sub>2</sub> and Co-N<sub>4</sub>. Therefore, our calculations reveal that the unique near-Fermi electronic structures of Co- $N_3C_1$  before and after  $O_2$  adsorption lead to its superior ORR performance, consistent with our experimental findings.

To address kinetic constraints for the further improvement of the ORR performance, we designed a core-shell-structured Co-N<sub>3</sub>C<sub>1</sub>@GC to enhance the mass transport and electron transfer processes. The heteroepitaxial growth of the coreshell Co/Zn-ZIF@ZIF-67 precursor toward the synthesis of the core-shell Co-N<sub>3</sub>C<sub>1</sub>@GC catalyst is illustrated in Scheme 1. Co/Zn-ZIF and ZIF-67 possess isoreticular structures with a similar unit cell, which is further confirmed by XRD (Figure S6).<sup>39,40</sup> The structural similarities of these two possible ZIF candidates allow for a sequential epitaxial growth of the coreshell structure (Co/Zn-ZIF@ZIF-67). The inner Co/Zn-ZIF core can be obtained by the homogenous coordination of both



Figure 3. (a) STEM-EDS elemental maps of the heterostructured Co/Zn-ZIF@ZIF-67 crystals. (b) SEM and (c) TEM images of the Co/Zn-ZIF@ZIF-67 crystal thermally derived Co-N<sub>3</sub>C<sub>1</sub>@GC catalysts. (d) Magnified aberration-corrected STEM-ADF image of the core–shell interface with some single Co atoms circled and carbon nanotube (CNT) marked. The Co K-edge of (e) FT-EXAFS and (f) XANES of Co-N<sub>3</sub>C<sub>1</sub>, Co-N<sub>3</sub>C<sub>1</sub>@GC, and GC. (g) The corresponding XANES fitting curves for Co-N<sub>3</sub>C<sub>1</sub>@GC.



**Figure 4.** (a) LSV curves of Co-N<sub>3</sub>C<sub>1</sub>, Co-N<sub>3</sub>C<sub>1</sub>@GC, and GC in an O<sub>2</sub>-saturated 0.1 M KOH solution at a sweep rate of 10 mV·S<sup>-1</sup> and an electrode rotation speed of 1600 rpm. (b) Corresponding Tafel plots obtained from the RDE polarization curves. (c) Electron transfer number (top) and H<sub>2</sub>O<sub>2</sub> yield (bottom) vs potential of Co-N<sub>3</sub>C<sub>1</sub>@GC. (d) LSV curves of Co-N<sub>3</sub>C<sub>1</sub>@GC before and after 5000 successive potential cycles. (e) A polarization curve and corresponding power density plot of the battery. (f) Stability test of a primary battery using the Co-N<sub>3</sub>C<sub>1</sub>@GC cathode catalyst at a current density of 10 mA·cm<sup>-2</sup> compared with the battery using Pt/C as the cathode catalyst.

Co<sup>2+</sup> and Zn<sup>2+</sup> with MeIm linkers. Subsequently, the inner core seeds the epitaxial growth of the ZIF-67 shell when a methanolic solution of a single-ion Co(NO<sub>3</sub>)<sub>2</sub> source is added into the growth reactor. All of the ZIF precursors synthesized here including Co/Zn-ZIF, ZIF-67, and core-shell Co/Zn-ZIF@ZIF-67 structures adopt the well-defined rhombic dodecahedral geometry, as evidenced by SEM (Figure S7) and TEM (Figure S8) imaging. EDS (Figure 3a) elemental mapping images reveal that Zn and Co species are mainly distributed at the inner core and outer shell regions, suggesting the successful synthesis of the heterostructured core-shell Co/ Zn-ZIF@ZIF-67. All of these samples exhibit similar Brunauer–Emmett–Teller surface areas (Figure S9a) and the same pore sizes (Figure S9b), which further confirms the heteroepitaxial growth of ZIF-67 on the surface of Co/Zn-ZIF.

The core-shell Co-N<sub>3</sub>C<sub>1</sub>@GC materials can be obtained by the thermal pyrolysis of Co/Zn-ZIF@ZIF-67 at 900 °C in argon flow, followed by acid etching to remove any accessible Co nanoparticles decorated on the shell. We note that direct pyrolysis of ZIF-67 and Co/Zn-ZIF precursors produces GC and Co-N<sub>3</sub>C<sub>1</sub> samples, respectively. In the former case, the formation of high density of thermally aggregated Co nanoparticles catalyzes the graphitization of organic linkers to produce highly crystallized carbon materials.41,42 In the latter case, we observed that an increase in the amount of Zn species generally favors the formation of Co-N<sub>3</sub>C<sub>1</sub> upon thermal annealing. This is because Zn ions tend to evaporate and Co ions can be reduced by carbonized organic linkers at an elevated temperature, resulting in the formation of atomically dispersed single Co atoms on a N-doped carbon support. The Co-N<sub>3</sub>C<sub>1</sub> sample derived from Co/Zn-ZIF (Figures S10 and 11) not only retains the original rhombic dodecahedron shape and size but also exhibits a smooth surface morphology without any large pore or crack, consistent with previous studies.<sup>19</sup> In contrast, the Co-N<sub>3</sub>C<sub>1</sub>@GC (Figures 3b,c and S12 and S13) prepared from Co/Zn-ZIF@ZIF-67 shrinks significantly upon thermal pyrolysis, resulting in a distorted, bumpy surface decorated with an abundance of carbon

nanotubes (CNTs) and graphitic walls. We also note that the pyrolysis treatment of the ZIF-67 alone (Figure S14) fails to produce CNTs. This suggests that unique heterostructured core-shell ZIFs promote the growth of CNTs during the pyrolysis process, presumably due to the formation of smallsized Co nanoparticles catalytically active for the growth of CNTs.<sup>43</sup> XRD measurements also reveal that Co-N<sub>3</sub>C<sub>1</sub> exhibits a broad shoulder peak in the range of  $20-30^{\circ}$ , corresponding to the (002) diffraction peak of relatively amorphous carbon (Figure S15). In contrast, both Co-N<sub>3</sub>C<sub>1</sub>@GC and GC samples exhibit the sharp features peaked at around 26 and  $44^{\circ}$ , corresponding to the (002) and (101) facets of graphitic carbon.<sup>44</sup> In addition, three weak features peaked at around 44, 51, and 76° can be assigned to the (111), (200), and (220)facets of face-centered-cubic (fcc) Co nanoparticles.<sup>45</sup> This is due to the presence of residual Co nanoparticles fully enclosed by graphitic layers in these samples, which cannot be removed by acid leaching.

A representative large-area STEM-ADF image (Figure S16) reveals that the Co-N<sub>3</sub>C<sub>1</sub>@GC sample exhibits a hollow polyhedron shape with a rough surface anchored with a high density of CNTs and graphitic fringes with an interplanar distance of ~0.34 nm. We note that the vast majority of the Co nanoparticles present in both Co-N<sub>3</sub>C<sub>1</sub>@GC and GC samples for catalyzing the crystallization of carbon can be removed by acid leaching treatment, aside from carbon-enveloped nanoparticles that are inaccessible to reactants (Figures S17-S20).<sup>42</sup> As shown in Figure 3d, a high density of Co single atoms is present in the inner N-doped amorphous carbon region but absent in the outer GC shell region. This is because a high crystallinity of graphitic carbon generally disfavors the immobilization of single Co atoms.<sup>16</sup> The FT of Co K-edge EXAFS spectrum (Figure 3e) of  $Co-N_3C_1$  exhibits a prominent peak at ca. 1.4 Å, attributed to the Co-N(C) coordination bond. The absence of a Co-Co peak at a higher R value confirms the atomic dispersion of single Co atoms of Co-N<sub>3</sub>C<sub>1</sub> even at a high metal loading of 2.1 wt % (measured by inductively coupled plasma optical emission spectroscopy). The ZIF-76-derived GC sample does show a major peak at 2.16 Å associated with the Co–Co bond, indicating that all of the Co atoms aggregate into the metallic nanoparticles. We also observe coexistence of the Co-N(C)- and Co-Co-bondrelated peaks for the core-shell-structured Co-N<sub>3</sub>C<sub>1</sub>@GC sample, arising from Co-N<sub>3</sub>C<sub>1</sub> core and metallic particles enclosed in the shell of GC, respectively. In the XANES spectrum (Figure 3f), the pre-edge for the GC sample nearly overlaps with that of Co foil, suggesting a metallic nature of Co particles. This is further supported by a linear combination fitting of Co K-edge XANES spectrum of Co-N<sub>3</sub>C<sub>1</sub>@GC with that of Co-N<sub>3</sub>C<sub>1</sub> and GC as two fitting components (Figure 3g). All of these results confirm the successful synthesis of core-shell-structured Co-N<sub>3</sub>C<sub>1</sub> wrapped by highly graphitized carbon through a pyrolysis treatment of heterostructured Co/ Zn-ZIF@ZIF-67 crystals. These CNTs and graphitic walls with excellent electrical conductivity facilitate the electron transfer from the electrode to the active materials and between active materials. Furthermore, it was also found that the outer shell shows a distinct mesoporous structure with the bumpy surface, which favors the diffusion of oxygen molecules toward the inner active sites.

The surface area and pore-size distributions in these samples were also investigated by performing N<sub>2</sub> adsorptiondesorption isotherms (Figure S21). The sharp uptakes at low relative pressure (<0.05) confirm the presence of micropores for all of the samples. In addition, the hysteresis loop and the gradual uptake at a relative pressure range from 0.45 to 1.0 observed for the Co-N<sub>3</sub>C<sub>1</sub>@GC sample arises from the capillary condensation of N<sub>2</sub> due to the presence of mesoscale pores with broad size distributions.<sup>46,47</sup> Aside from the presence of the conducting GC shells, Co-N<sub>3</sub>C<sub>1</sub>@GC samples also possess a large pore volume and a high surface area of 862 m<sup>2</sup>·g<sup>-1</sup>. Such a core—shell SAC with a hierarchically micro/ mesoporous structure not only hosts sufficiently high density of active sites (Co-N<sub>3</sub>C<sub>1</sub>) but also provides sufficient channels for the electrolyte to boost the mass transport and electron transfer in the electrocatalysis.

As shown in Figure 4a, despite a higher electrical conductivity, the GC sample exhibits a poor ORR activity due to the lack of single Co active sites. Among all of these samples, the Co-N<sub>3</sub>C<sub>1</sub>@GC offers the best ORR activity with a more positive half-wave potential of 0.846 V (vs RHE) (Figure S22), smaller Tafel slope of 46 mV·dec<sup>-1</sup> (Figure 4b), and larger diffusion-limited current density of 5.16 mA·cm<sup>-2</sup>, superior to those of most non-noble-metal electrocatalysts. It is worth mentioning that both Co-N<sub>3</sub>C<sub>1</sub>@GC and Co-N<sub>3</sub>C<sub>1</sub> catalysts present the same onset potential because they contain the same single Co active sites. However, the mass transport and electron transfer for the core-shell Co-N<sub>3</sub>C<sub>1</sub>@GC catalyst can be greatly accelerated due to the wrapping of the mesoporous graphitic carbon shell, leading to a much large diffusion-limited current density and a lower Tafel slope, compared to the commercial Pt/C catalyst (Figures S23 and S24). We also obtained the Koutecky–Levich (K-L) plots for Co-N<sub>3</sub>C<sub>1</sub>@GC based on the measurement of RDE polarization curves at different rotating speeds ranging from 900 to 2500 rpm (Figure S25). Such a plot shows nearly parallel fitting lines, suggesting a first-order reaction kinetics with respect to O<sub>2</sub> concentration and a potential-independent electron transfer rate. The high electron transfer rate is further evidenced by the RRDE test results (Figure 4c). It demonstrates a four-electron ORR pathway over the active sites of Co-N<sub>3</sub>C<sub>1</sub>@GC. The

durability of Co-N<sub>3</sub>C<sub>1</sub>@GC was assessed by cycling the catalyst between 0.4 and 1.0 V at a sweep rate of 50 mV·s<sup>-1</sup> in the O<sub>2</sub>-saturated 0.1 M KOH solution.  $E_{1/2}$  shows a negligible decay after 5000 continuous potential cycles (Figure 4d), which demonstrates an excellent durability of the Co-N<sub>3</sub>C<sub>1</sub>@ GC catalyst in the operation conditions.

In addition, we also fabricate a primary Zn-air battery consisting of Co-N<sub>3</sub>C<sub>1</sub>-SACs dropped on the carbon paper electrode as the air cathode and a Zn foil in 6 M KOH solution as the anode. As shown in Figure 4e, the battery shows an open circuit voltage of ~1.40 V. Moreover, the Co-N<sub>3</sub>C<sub>1</sub>@GC catalyst delivers a peak power density of 255 mW·cm<sup>-2</sup>, much higher than that of Co-N<sub>3</sub>C<sub>1</sub>, and slightly outperformed the battery using a Pt/C catalyst with the same mass loading. Such an outstanding battery performance of the Co-N<sub>3</sub>C<sub>1</sub>@GC cathode catalyst can be correlated to the elaborately designed core—shell structure, which facilitates the O<sub>2</sub> diffusion and fast electron transfer at the electrode. After a long-term galvanostatic discharge at 10 mA·cm<sup>-2</sup> for 10 h, no obvious voltage drop was observed, owing to the high stability of Co-N<sub>3</sub>C<sub>1</sub>@GC for ORR (Figure 4f).

## CONCLUSIONS

In conclusion, we have demonstrated that both the local and global structures of CoN<sub>r</sub> SACs have a profound impact on their electrocatalytic performance. We designed a core-shellstructured Co-N<sub>3</sub>C<sub>1</sub>@GC catalyst that integrates a high density of locally optimized single Co active sites  $(Co-N_3C_1)$ enveloped by a globally engineered porous and conductive carbon network through direct carbonization of heterostructured Co/Zn-ZIF@ZIF-67 crystals. The catalyst exhibits an outstanding ORR performance with a positive half-wave potential of 0.846 V, small Tafel slope of 46 mV dec<sup>-1</sup>, and high durability (5000 cycles). The rational design of a coreshell Co-N<sub>3</sub>C<sub>1</sub>@GC catalyst can simultaneously overcome the thermodynamic and kinetic constraints for efficient electrochemical reactions. Our results not only offer a new route for the optimization of the electrochemical performance of carbon-based SACs but also provide new insights into artificially designed SAECs for key electrochemical transformations.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c00936.

SEM images, TEM images, XRD patterns, XPS data, and ORR activities; aberration-corrected STEM-ADF images of Co-N<sub>3</sub>C<sub>1</sub> in different spatial locations; Co K-edge EXAFS fitting curves; linear sweep voltammetry curves of Zn-NC and Co-N<sub>3</sub>C<sub>1</sub> in an O<sub>2</sub>-saturated 0.1 M KOH solution; reaction energy diagram of Co-N<sub>4</sub>, Co-N<sub>3</sub>C<sub>1</sub>, and Co-N<sub>2</sub>C<sub>2</sub>; XRD patterns of Co/Zn-ZIF, Co/Zn-ZIF @ZIF-67, and ZIF-67; and SEM images of assynthesized Co-N<sub>3</sub>C<sub>1</sub> (PDF)

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## **Author Contributions**

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The authors declare no competing financial interest.

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