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# Spatial Isolation of Zeolitic Imidazole Frameworks-Derived Cobalt Catalysts: From Nanoparticle, Atomic Cluster to Single Atom

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Xiaopeng Han, Xiaofei Ling, Ying Wang, Tianyi Ma, Cheng Zhong, Wenbin Hu, Yida Deng\*

Abstract: The size effect of transition metal nanoparticles on electrocatalytic performance remains ambiguous especially when decreasing the size to atomic level. Herein, we report the spatial isolation of cobalt species at atomic scale through tuning zinc dopants content in predesigned bimetallic Zn/Co zeolitic imidazole frameworks (ZnCo-ZIFs), affording the successful synthesis of nanoparticles, atomic clusters and single atoms of Co catalysts on N-doped porous carbon. This novel synthetic strategy allows the investigation of size effect on electrochemical behaviours from nanometer to angstrom. Electrochemical results demonstrate that the single Co atomic catalyst manifests superior bifunctional ORR/OER activity, durability and reversibility for Zn-air batteries in comparison with other counterparts and noble metal Pt/C+RuO<sub>2</sub>, which can be attributed to the isolated single Co atoms with high reactivity and stability. Our findings open up a new avenue to regulate the metal particle size and catalytic performance of metal-organic framework derivatives at multiscale level.

Understanding the size effect of nanoparticle catalysts on their activities is one of the main research topics in establishing structure-reactivity correlations in the field of heterogeneous catalysis.<sup>[1]</sup> Particularly, single-atom catalysts are emerging as a new research frontier,<sup>[2]</sup> featuring minimum particle size and maximum utilization of coordinately unsaturated metal sites. On the other hand, electrocatalytic oxygen reduction/evolution reactions (ORR/OER) are important coupled redox reactions that are related to various electrochemical energy conversion systems, such as fuel cells, metal-air batteries and water-spiltting devices,<sup>[3]</sup> etc. Regarding the investigation of size effect on ORR activity, much effort has been devoted to Pt-based catalysts since reducing the particle size and increasing the mass/specific activities are essential tasks for the efficient uilization of this precious resource.[4] To completely subtitute precious metals, transition metal (TM, e.g., Co, Ni, Fe) catalysts have aroused increasing interests owing to their natural advantages of low cost. high abundance, remarkable structural stability and potential bifunctionality.<sup>[3a, 5]</sup> However, to the best of our knowledge, although various studies of TM particle size effects are displayed in traditional catalysis (e.g., cobalt particle size effects for Fischer-Tropsch (FT) reaction),<sup>[6]</sup> little work has been done to systematically demonstrate the size influence on ORR/OER performance of well-defined TM-based catalysts. Moreover, the particle size in aforementioned metal-based nanomaterials is generally restricated in the range of approximately 1 to 20 nm by the conventional preparation methods like thermal treatment,<sup>[5c, 7]</sup>

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chemical reduction route,<sup>[8]</sup> and impregnation method,<sup>[1b, 9]</sup> which results in a great challenge to clarify the influence of crystal size on electrocatalytic properties over a wide size ranging from nanoparticles to nanoclusters and even single atoms.

Recently, zeolitic imidazole frameworks (ZIFs), a subclass of metal-organic frameworks (MOFs), have been considered as suitable precursors to synthesize transition metal and N-doped porous carbon (TM-N-C) composite materials via a pyrolysis process.<sup>[2a, 10]</sup> The increased number of coupled TM-N<sub>x</sub> active sites and simultaneously enhanced reactivity of active moieties are responsible for the remarkable catalytic performance of resultant TM-N-C electrocatalysts.<sup>[2b, 5a]</sup> Notably, bimetallic active sites can be introduced to further enhance the ORR activity by adding bimetallic cations during the growth of ZIFs.<sup>[5b]</sup> Meanwhile, the homogeneous dopants of secondary metal atoms in the MOFs can facilitate the tuning of coordination environment of metallic centers and also provide steric hindrance for potential agglomeration during pyrolysis.<sup>[5a]</sup> Notwithstanding, on the one hand, the specific isolation mechanism has not been systematically understood so far; on the other hand, seldom work has achieved the tuning and preparing of multiscale TM particles from nanometer to angstrom, which is essential to identify the size influence of MOFs-derived materials on electrocatalytic properties.



Figure 1. Schematic illustration of the preparation procedures of Co-NPs@NC, Co-ACs@NC and Co-SAs@NC catalysts.

Herein, we realized the spatial isolation of cobalt species at atomic level through tuning zinc dopants content in bimetallic ZnCo-ZIFs precursors, giving Co nanoparticles, atomic Co clusters and Co single atoms on N-doped carbon, designated as Co-NPs@NC, Co-ACs@NC and Co-SAs@NC, respectively. The developed novel strategy allows the investigation of size influence on electrochemical activity of TM catalysts with the size down to single atomic scale. Specifically, by precisely regulating the Zn/Co molar ratios in ZIFs structures, Co atoms can be geometrically separated to different extents by the introduced Zn atoms upon pyrolysis with lowest isolation degree for nanoparticles (Zn:Co=0:1), moderate degree for atomic clusters (Zn:Co=2:1) and highest degree for single atoms (Zn:Co=8:1), as schematically

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# illustrated in **Figure 1**. Among them, Co-SAs@NC exhibits the best ORR activity in terms of highest onset potential (0.96 V), highest half-wave potential (0.82 V) and largest kinetic current density (15.2 mA cm<sup>-2</sup>), closely approaching that of commercial Pt/C (0.98 V, 0.82 V, 15.7 mA cm<sup>-2</sup>). Furthermore, Co-SAs@NC also displays outstanding long-term durability and reversibility for Zn-air batteries, superior to noble metal Pt/C+RuO<sub>2</sub>.

ZnCo-ZIFs were synthesized via the sodalite coordination of  $Co^{2+}$  and  $Zn^{2+}$  nodes with 2-methylimidazole in methanol. Three samples with Zn/Co molar ratios of 0, 2 and 8 were obtained, designated as Co-ZIF, ZnCo-ZIF-2 and ZnCo-ZIF-8, respectively. Compared to pure Co-ZIFs, the introduced Zn<sup>2+</sup> dopants partially replace the original Co<sup>2+</sup> ions in ZnCo-ZIFs, thus the spatial isolation of cobalt species is effectively realized at atomic level.<sup>[2a]</sup> The X-ray powder diffraction (XRD) patterns of as-prepared ZnCo-ZIFs were well matched with simulated ZIFs (Figure S1), confirming the Zn-doping nature. Scanning electron microscope

(SEM) images showed the dodecagon shape of prepared ZnCo-ZIFs (Figure S2). After pyrolysis at 1173 K under Ar atmosphere, the organic linkers were carbonized into N-doped porous carbon and Zn species with low boiling point was evaporated at such a high temperature while Co particles were remained and anchored on N-doped carbon support.<sup>[2a]</sup> In the XRD curves of resultant composites (Figure S3), only two broad peaks were observed in the range of 20°-50°, which can be assigned to the (002) and (100) planes of graphitic carbon. Further morphological characterizations revealed the highly dispersed and dodecagonal nanostructures that were inherited from the initial ZIFs precursors (Figure S4). The products were subsequently refluxed in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution to remove the possible inactive and unstable metal species. Co-NPs@NC, Co-ACs@NC and Co-SAs@NC nanocomposites were finally received with no XRD signals of Co



Figure 2. (a) SEM, (b) TEM, (c) elemental mapping of Co-SAs@NC. (d) TEM image of Co-NPs@NC. Inset shows the HRTEM of an individual particle. (e, f) HAADF-STEM images of (e) Co-ACs@NC and (f) Co-SAs@NC. (g) N<sub>2</sub> adsorption-desorption isotherm curves. (h) Co XANES spectra of Co-SAs@NC, Co foil and CoO. (i) Fourier-transforms of Co K-edge spectra of Co-SAs@NC and Co foil.

The size and morphology of ZIFs were maintained after acid leaching in the resultant three hybrids while their surface became rougher with the presence of obvious porous structures (Figures 2a, b and S6, S7). Elemental mapping of Co-SAs@NC reveals the homogeneous dispersion of C, N and Co species over the entire nanoarchitecture (Figure 2c). Transmission electron microscopy (TEM) indicates the formation of Co nanoparticles by thermal treatment of pure Co-ZIFs without the isolation of Zn (Figure 2d), which is confirmed by the observed lattice distance of 0.26 nm in the high resolution TEM (HRTEM, inset of Figure 2d), consistent with the spacing between the (101) plane of metallic Co. Aberration-corrected high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images show the generation of Co atomic clusters and single atoms from pyrolyzed bimetallic ZnCo-ZIFs with increased Zn/Co molar ratios of 2:1 and 8:1 (Figure 2e, f), clearly verifying

the spatial isolation effect of doped zinc atoms. As a result, the mixed Zn acts as a "fence" to expand the distance of adjacent Co atoms in space, rendering the multiscale controllable synthesis of different aggregation degree of atomic Co. The N<sub>2</sub> adsorption-desorption isotherms resemble type IV (Figure 2g), indicating the appearance of mesopores after acid etching, which is further supported by the pore size distribution curves (Figure S8). Brunauer-Emmett-Teller (BET) values are characterized to be 180.1, 98.8, and 130.7 m<sup>2</sup> g<sup>-1</sup> for Co-NPs@NC, Co-ACs@NC, and Co-SAs@NC products. The large specific surface area and rich porous structure are expected to facilitate the gas diffusion and ion transportation, contributing to the enhanced catalytic activity. Raman spectra reveal that all the  $I_{D}/I_{\rm G}$  ratios ( $I_{\rm D}$  and  $I_{\rm G}$  represent the intensity of D- and G-bands of carbon materials) are 0.98 (Figure S9), suggesting the same graphitic structures in three hybrids. This allows the exclusion of

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influence of carbon supports on the catalytic performance, focusing on the difference from Co size and configuration. Synchrotron X-ray absorption spectroscopy analysis was performed to further identify the atomic structures in the synthesized hybrids. Figure 1h presents the Co K-edge X-ray absorption near-edge structure curves. The comparison with reference CoO and Co foil implies that the Co single atoms in Co-SAs@NC are positively charged, in good agreement with previous observations.<sup>[2a, 11]</sup> Fourier transform profile of Co-SAs@NC in Figure 1i presents a primary peak at 1.47 Å, corresponding to Co-N scattering path, which is also corroborated by the X-ray photoelectron spectroscopy (XPS) results (Figure S10). Compared with the spectra of Co-ACs@NC and Co foil (Figure S11), no Co-Co path at around 2.1 Å is observed in Co-SAs@NC, an indication of the atomically dispersed Co single atoms.<sup>[4a, 11]</sup> According to Inductively coupled plasma-mass spectrometry (ICP-MS) analysis, the mass percentages of anchored metallic Co species are 4.91, 3.95, and 1.70 wt% for Co-NPs@NC, Co-ACs@NC, and Co-SAs@NC catalysts, respectively. These aforementioned results collectively demonstrate the successful synthesis of metallic Co catalysts with different particle size, highlighting the pivotal role of Zn dopants in regulating the spatial isolation of Co atoms.



**Figure 3.** (a) ORR polarization curves measured using RRDEs at 1600 rpm and (b)  $J_k$  at 0.6 V and  $E_{1/2}$  for synthesized Co-NPs@NC, Co-ACs@NC, Co-SAs@NC and Pt/C catalysts. (c) Corresponding percentage of peroxide and electron transfer number. (d) Polarization curves of Co-SAs@NC at different rotation rates. Inset shows the K-L plots. (e) Dependence of current densities as a function of scan rates at 0.40 V. (f) Chronoamperometric curves of Co-SAs@NC at 0.6 V vs RHE. Inset shows the prolonged CVs of Co-SAs@NC at 400 rpm at a scan rate of 250 mV s<sup>-1</sup>.

The formation of series catalysts inspires us to investigate the multiscale size effect on their electrocatalytic properties. Rotational ring-disk electrodes (RRDEs) were employed to assess the ORR activity of synthesized composites in O<sub>2</sub>-saturated 0.1 M KOH. As shown in **Figures 3**a, b and Table S1, Co-SAs@NC exhibits superior catalytic activity in terms of higher onset potential ( $E_{onset}$ , 0.96 V), higher half-wave potential ( $E_{1/2}$ , 0.82 V) and larger limiting diffusion current density ( $J_{d}$ , 4.96 mA cm<sup>-2</sup>), which significantly outperforms those of Co-ACs@NC (0.91 V, 0.81 V, 4.44 mA cm<sup>-2</sup>) and Co-NPs@NC (0.90 V, 0.80 V, 3.86 mA cm<sup>-2</sup>), and also surpasses that of most precious metal-free electrocatalysts reported to date (Table S2). After correcting the diffusion-limited current by Koutecky-Levich (K-L)

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equation, the calculated kinetic current densities  $(J_k)$  of Co-NPs@NC, Co-ACs@NC, Co-SAs@NC and Pt/C were 7.1, 10.6, 15.2 and 15.7 mA cm<sup>-2</sup> at 0.6 V, indicating the fast reaction kinetics on Co-SAs@NC. The ORR catalytic performance was also gleaned by the determined electron transfer number (n) and yield of peroxide generation (y). As illustrated in Figure 3c, the monitored n of Co-SAs@NC is above 3.9 and peroxide percentage is below 3% over the potential range of 0.2-0.85 V, demonstrating that Co-SAs@NC catalyzed ORR via an apparent 4e<sup>-</sup> mechanism, similar to Pt/C, which is recognized to be a highly efficient reaction pathway. This is also certified by the results from K-L determination (Figures 3d and S12). The lower n and higher y values on Co-ACs@NC and Co-NPs@NC suggest the ORR activities following the trend of Co-SAs@NC > Co-ACs@NC > Co-NPs@NC. Electrochemical active surface areas (ECSA) of 19.1, 39.2, 51.4 mF cm<sup>-2</sup> for Co-NPs@NC, Co-ACs@NC and Co-SAs@NC (Figure 3e) further reveals the advantage of Co single atoms in providing more catalytically active sites and high atomic utilization for oxygen adsorption and subsequent reactions, acting as a critical factor for the substantially enhanced ORR activity. This is also confirmed by the highest mass activity of Co-SA@NC catalyst (Figure S13). Moreover, electrochemical impedance spectroscopy (EIS) discloses the smallest charge transfer resistance on Co-SAs@NC during the catalytic process (Figure S14), resulting in the fast reaction kinetics. Notably, the acid etching can also benefit the ORR improvement by increasing the surface roughness and the electrochemical active area (Figures S15, S16 and Table S1). The remarkable ORR performance of Co-SAs@NC catalyst can also be observed in either acidic or neutral electrolytes (Figure S17), demonstrating its universal catalytic capability for different practical environments. Furthermore, preliminary results show that Co-SAs@NC also exhibits remarkable OER activity (Figure S18), making it as a promising bifunctional catalyst that plays an important role in rechargeable metal-air batteries. Apart from high catalytic activity, Co-SAs@NC hybrid also affords excellent long-term operation durability. After a continuous chronoamperometric period of 22.5 h, the cathodic current retention of Co-SAs@NC is much higher than that of Pt/C (94.4 % vs 79.2 %, Figure 3f). The remarkable catalytic stability is further corroborated by almost overlapped CV curves after extended 5,000 cycles (the inset of Figure 3f). Additionally, in a sharp contrast to Pt/C, the Co-SAs@NC hybird shows considerable methanol tolerance (Figure S19), implying its potential application for methanol fuel cells.

A homemade Zn-air battery was further assembled to assess the electrochemical performance of synthesized materials under real operation conditions with zinc plate as the anode, Co-based catalysts as the air cathode, and 6.0 M KOH and 0.2 M ZnCl<sub>2</sub> as the electrolyte (Figure 4a). The Co-SAs@NC based battery can work with an open-circuit voltage (OCV) of 1.46 V (Figures 4b and S20), higher than that involving Co-ACs@NC (1.38 V), Co-NPs@NC (1.37 V) and Pt/C (1.41 V). The voltage-current polarization curves indicate the best performance of Co-SAs@NC cathode among three hybrid catalysts (Figure 4c), which even surpasses that of the Pt/C-based battery at current density below 100 mA cm<sup>-2</sup>. The highest power density is achieved on battery using the Co-SAs@NC electrode (105.3 mW cm<sup>-2</sup> at 158 mA cm<sup>-2</sup>), approaching to that of the Pt/C (110.4 mW cm<sup>-2</sup> at 184 mA cm<sup>-2</sup>). For a primary battery setup, the battery catalyzed by Co-SAs@NC delivers a discharge specific capacity of 897.1 mA h  $g^{-1}$  at 20 mA cm<sup>-2</sup> based on the mass of consumed Zn (Figure 4d), much larger than that of Pt/C (783.5 mA h  $g^{-1}$ ). The rechargeable performance of the Co-SAs@NC-based Zn-air battery was also evaluated (Figure S21), which gives a superior reversibility over Pt/C+RuO<sub>2</sub> counterpart and rivals the electrocatalysts reported previously (Table S3).<sup>[12]</sup>

To explore the potential application in portable and wearable devices, a flexible solid-state Zn-air battery was constructed by zinc foil anode, KOH-poly(vinyl alcohol) (PVA) electrolyte and carbon cloth supported Co-SAs@NC cathode (Figure 4e). A

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**Figure 4.** (a) Schematic illustration of aqueous Zn–air battery. (b) Open-circuit voltages, (c) polarization curves and corresponding power densities of Co-NPs@NC, Co-ACs@NC, Co-SAs@NC and Pt/C-based Zn-air batteries. (d) Discharge curves of primary Zn-air batteries catalyzed by Co-SAs@NC and Pt/C at 20 mA cm<sup>2</sup>. (e) Structural illustration of solid-state Zn-air battery. (f) Discharge–charge performance of flexible Zn-air batteries. (g) Photographs of LED screen lighted by two batteries connected in series using Co-SAs@NC catalyst. (h) Cycling performance of the battery with Co-SAs@NC cathode at different bending angles at 2 mA cm<sup>2</sup>.

high OCV of 1.40 V is obtained (Figure S22), comparable to the value in aqueous system. The galvanostatic discharge-charge profiles in Figure 4f suggest that the stable voltage plateau can be maintained well for 1000 min at a current density of 1 mA cm<sup>2</sup>, 700 min at 2 mA cm<sup>-2</sup> (20 min per cycle). As a demo, two flexible batteries connected in series can power a red light-emitting diode (LED) screen (Figure 4g) and also are capable of maintaining extremely stable discharge-charge platforms at different bending angles (Figure 4h), demonstrating the considerable flexibility.

The outstanding electrocatalytic performance of the Co-SAs@NC catalyst is attributed to the following factors. First, the isolated single Co atoms provide maximized atomic utilization and more catalytic sites with superior reactivity.<sup>[11]</sup> Meanwhile, the coordination with N species in N-doped carbon support ensures the stabilization of Co-SAs.<sup>[2a]</sup> The second reason is that the large surface area and mesoporous structure of the carbon matrix affords the exposure of accessible atomic sites and the fast diffusion of O<sub>2</sub> and electrolyte. Finally, high conductivity of the carbon framework also favors the catalytic process by enhancing the efficient electron transport.

In summary, this work demonstrates the controlled synthesis of multiscale Co metallic catalysts through regulating the spatial isolation of Co species by heteroatom Zn doping and investigates their size-dependent electrocatalytic properties. The Co single atoms anchored on N-doped carbon hybrid delivers outstanding bifunctional activity, catalytic durability and reversibility for Zn-air batteries, that is superior to most of the precious and transition metal-based catalysts. Further investigations highlight the isolated single atomic sites with high reactivity and stability in facilitating the remarkable catalytic activities. These findings should shed light on the regulation of particle size through spatial separation and improves our understanding on the size-performance effect of atomically dispersed materials for chemical and electrochemical reactions.

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**Keywords:** Size effect, Single atoms, Electrocatalysis, ORR, Metal-air battery

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We report the regulation of Co atoms through spatial isolation by heteroatom Zn doping in bimetallic ZnCo-ZIFs, enabling the tunable particle size from nanoparticles, atomic clusters to single atoms supported on N-doped carbon, among which the single atoms catalyst exhibits superior electrocatalytic activity, catalytic durability and reversibility for Zn-air battery owing to the isolated Co single atomic sites with high reactivity and durability.



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