

## **Accepted Article**

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201710852 Angew. Chem. 10.1002/ange.201710852

Link to VoR: http://dx.doi.org/10.1002/anie.201710852 http://dx.doi.org/10.1002/ange.201710852

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# Active Salt/Silica-Templated 2D Mesoporous FeCo-Nx-Carbon as Bi-functional Oxygen-Electrodes for Zn-Air Batteries

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Abstract: Heteroatom-doped carbons have received increasing interest in constructing next-generation reversible oxygen electrocatalysts for rechargeable Zn-air batteries. Even though many types of heteroatom- doped carbons have been reported, the rational design of heteroatom doped carbons with control of microand nanostructure, porosity and surface area, amount and dispersion of heteroatom and metal doping remains an enormous challenge. Here, two types of templates, an active salt and silica nanoparticles, are used concurrently to achieve the facile synthesis of hierarchical meso- microporous FeCo-Nx-carbon nanosheets (meso/micro-FeCo-Nx-CN) with highly dispersed metal sites. The resulting meso/micro-FeCo-Nx-CN shows high and reversible oxygen electrocatalytic performances for both ORR and OER, thus having potential for applications in rechargeable Zn-air battery. Our approach creates a new pathway to fabricate 2D meso/microporous-structured carbon architectures for bifunctional oxygen electrodes in rechargeable Zn-air battery as well as opens avenues to the scale-up production of rationally designed heteroatom-doped catalytic materials for a broad range of applications.

Rechargeable metal-air batteries are considered as one of the most promising candidates as power source for next generation electric vehicles and many other electrical devices because of their low cost and high energy density.<sup>[1]</sup> The efficiency of charge-discharge processes of metal-air batteries is significantly affected by the electrocatalysts for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), respectively. At present, one of the major challenges impeding the widespread commercialization of rechargeable metal-air batteries reside in the low onset and half-wave potential of ORR (i.e. determining the working discharge voltage of the battery) and high overpotential of OER (i.e. the charge voltage of the battery).<sup>[2]</sup> Precious metal based electrocatalysts (e.g. Pt/C, RuO<sub>2</sub>, Ir/C)) usually possess high catalytic activity either for ORR or OER. However, none of these commercial catalysts can satisfyingly perform both reactions. Furthermore, poor long-term durability caused by structural degradation or poisoning of catalytic centers during electrochemical operations also hinder their widespread applications.<sup>3</sup> Therefore, the development of highly efficient and durable non-precious metal based catalysts, which are simultaneously active for ORR and OER as bi-functional electrodes to accelerate the charge and discharge processes is inevitable for designing advanced rechargeable metal-air batteries, however remains a major challenge.

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Recent studies demonstrated that heteroatom-doped carbon nanomaterials are promising materials for bifunctional oxygen catalysts.<sup>[4]</sup> For example, a metal-free, N. P-doped carbon prepared by pyrolysis of a phytic acid containing polyaniline aerogel was described as bi-functional ORR/OER catalyst in Znair battery.<sup>5</sup> The catalyst showed a high ORR activity in term of a half-wave-potential of 0.85 V vs. RHE. However, the OER activity of such N. P-doped carbon metal free catalysts was less significant, resulting in an  $E_{gap}$  of ~1.0 V, while the  $E_{gap}$  indicates the potential difference between ORR half-wave-potential and OER potential at 10 mA/cm<sup>2</sup>. To improve the OER performance, metal-N<sub>x</sub>-carbon catalysts were widely investigated.<sup>[6]</sup> Zhang et al. reported a graphene based Co-Nx-C catalyst, which exhibited good ORR/OER bi-functional activities yielding an  $E_{gap}$  of ~0.95 V.<sup>6a</sup> Notably, while Co-Nx-doped carbons showed improved OER activity, this is paid-off by an inferior ORR activity. high-performance Therefore. achieve bi-functional to electrochemical catalyst, synergetic doping of a highly ORRactive and OER-active structures, such as bimetal Fe, Co, Ni, Mn or Zn-N<sub>x</sub> centers in one carbon catalysts has been proposed and investigated. However, even though several metal/heteroatom-doped carbons have been reported for reversible oxygen electrocatalysts, just few reports rationally discussed how nanoarchitecture, such as morphology and meso/micro-porosity of the carbon materials influence the reversible oxygen catalytic activity and stability. [3a, 8]

Owing to their unique properties compared with conventional porous carbon analogues, two-dimensional (2D) porous carbon nanosheets, are attracting increasing attention for their potential application in the fields of electronics, sensing, energy storage, and conversion, [3b, 9] especially because the 2D morphology with additional porosity increases the accessible surface area for the electrolyte, thus accelerating mass and charge transfer.[3b, 8b, 9a, <sup>10</sup> Recently, several synthetic methods for the preparation of 2D mesoporous carbon nanosheets have been reported, including hard and soft templating approaches using silica nanoparticles or amphiphilic block-co-polymers, respectively  $\overset{[\underline{9b}, \, \underline{11}]}{}$  However, a one-step method to produce not only facile 2D meso/microporous, but also bimetal-Nx-doped carbons, which can be applied as reversible ORR-OER catalysts has not been reported. This is possibly due to the lack of suitable and easilyscalable structure-directing agents to guide the assembly of 2D morphologies as well as the inner-connected bimetal-N<sub>x</sub> meso/micro-structures.

Here, we report the synergistic utilization of two types of templates, an active salt and silica nanoparticles, to achieve the facile synthesis of 2D meso/microporous Fe/Co-N<sub>x</sub>-doped carbon nanosheets with excellent reversible ORR-OER catalytic performance. In our approach, layered FeCl<sub>3</sub>·6H<sub>2</sub>O inorganic crystal are applied as 2D active salt template, which first coordinates with dopamine hydrochloride (DA) to form a layered organic-inorganic hybrid structure (Figure 1a).<sup>[9a]</sup> Subsequently, a certain amount of CoCl<sub>2</sub>·6H<sub>2</sub>O was added to enable Co doping. Furthermore, silica nanoparticles (Ludox AS-40, particle size of ~22 nm) were mixed with this paste by vigorous grinding until a

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homogenous mixture is observed (Figure S1). The resulting DAmetal salt-silica nanoparticle mixtures were thermally treated under an inert atmosphere to yield  $FeCo-N_x$ -doped carbons with encapsulated silica nanoparticles. The residual metal salts and silica templates were then removed by etching and washing, then a secondary thermal treatment was applied to yield the final products named meso/micro-FeCo-N\_x-CN. The amount of silica templates was varied to tailor the amount of mesoporosity in the carbon nanosheets. For comparison, carbon nanosheets without addition of silica nanoparticles were also prepared to yield entirely microporous materials (micro-FeCo-N<sub>x</sub>-CN) (see details in Table S1). All the meso/micro-FeCo-N<sub>x</sub>-CN catalysts discussed in the following part are synthesized with 30 wt.% silica (meso/micro-FeCo-N<sub>x</sub>-CN-30), if not noted otherwise.



Figure 1. a) Schematic illustration of the process of active salt/silica-templated 2D meso/micro-FeCo-N<sub>x</sub>-CN-30; b, c) SEM, d) TEM and e) HAADF-STEM images and the corresponding element mapping of C, N, Fe, and Co and f) high resolution HAADF-STEM images of meso/micro-FeCo-N<sub>x</sub>-CN-30.

The meso/micro-FeCo-Nx-CN-30 catalysts were investigated by scanning electron microscopy (SEM) (Figure 1). While micro-FeCo-Nx-CN synthesized without silica NP template, shows a uniform 2D nanosheet morphology (Figure S2) with smooth surface, addition of silica template (Figure 1 b-c) yield a pronounced mesoporous structure within the nanosheets. By varying the amount of silica template, the porosity and thickness of the pore walls can be adjusted. The morphology of meso/micro-FeCo-Nx-CN prepared with 20% and 40% template are shown in figure S3 and S4, both exhibiting a mesoporous structure as well. When higher amounts of silica template are applied (e.g. 40%), abundant mesopores are still visible, but the structure seem to be partially collapsing, probably due to pore wall thinning. (Figure S4). A silica amount of 30% thus seem to be ideal to reach high mesoporsity and structural stability. Atomic force microscopy (AFM) was conducted to verify the 2D morphologies and the thickness of the nanosheets (Figure S5). As shown in the AFM images, most of the as prepared micro-FeCo-Nx-CN shows thickness ranged from 15.2-24.3 nm, and the meso/micro-FeCo-Nx-CN shows a thickness of about 48.5

nm. Besides the increased thickness, the meso/micro-FeCo-Nx- CN also shows increased surface roughness due to its mesoporous structures.

To further identify the morphology and element distribution on the mesoporous carbon nanosheets, transmission electron microscopy (TEM), high angle annular dark-field scanning transmission electron microscope (HAADF-STEM), high resolution STEM (HR-STEM), and TEM elemental mapping were measured. The TEM image in Figure 1d shows a thin nanosheet with uniformly distributed mesoporous structures. The HAADF TEM image (Figure 1e) and corresponding elemental mapping of C, N, Fe, and Co reveals again the 2D morphology and the uniform distribution of C, N, Fe, and Co elements within the meso/micro-FeCo-Nx-CN nanosheets, indicating homogeneous doping and distribution of active centers on the catalyst. Metal distribution within the meso/micro-FeCo-Nx-CN were further investigated by HAADF-STEM (Figure 1f). Within the pore walls, very small isolated bright dots, with diameters of 0.1-0.2 nm can be identified, attributable to single or multi-metal atoms doping in the catalyst. It was reported that this kind of single or multi-

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atoms doping is favorable for the formation of Metal-Nx active cen

centers, therefore enhancing the performance of the catalyst.<sup>[12]</sup>



Figure 2. a)  $N_2$  adsorption/desorption isotherms, b) calculated mesoporous surface area from t-plot of the as prepared materials; c) pore size distribution curves calculated from the adsorption branch of the isotherms by the QSDFT model.

The porous characteristics for the materials were further analyzed by nitrogen sorption measurements. The calculated Brunauer-Emmett-Teller (BET) surface areas of micro-FeCo-Nx-CN and meso/micro-FeCo-Nx-CN-20, 30 and 40 are 1025, 1120, 1168 and 1321 m<sup>2</sup>/g, respectively. The N<sub>2</sub> adsorption/desorption measurements (Figure 2a) for micro-FeCo-Nx-CN shows a type I isotherm, i.e. an explicitly microporous pore structure. For meso/micro-FeCo-Nx-CNs the isotherms change to type IV showing that an additional mesoporosity was successfully introduced by the silica template. The mesoporous surface area of micro-FeCo-N<sub>x</sub>-CN and meso/micro-FeCo-N<sub>x</sub>-CN-20, 30, 40 calculated from the t-plot are 124, 459, 652 and 832 m<sup>2</sup>/g (Figure 2b). These measurements show that addition of silica template does not significantly change the surface area but rather increase the fraction of meso- to micropores. The pore size distribution was analyzed by the QSDFT model to calculate the micropore size and mesopore size separately (Figure 2c). Meso/micro-FeCo-N<sub>x</sub>-CN-30 shows some amount of micropores and mesopores, while for the latter a maximum pore width is seen around 20 nm, reflecting the size of the silica nanoparticle template. In contrast to micro-FeCo-Nx-CN very small pores in the micropore region (<0.7 nm) have significantly decreased, explaining the low change in overall surface area. Also for meso/micro-FeCo-Nx-CN-20 abundant mesopores are visible, again with a maximum at ~ 20 nm pore diameter, while for meso/micro-FeCo-N<sub>x</sub>-CN-40 a broader pore size distribution is observed, pointing to the partial collapse of the mesopores structure due to the thinning of the pore walls. (Figure S6).

X-ray photoelectron spectroscopy (XPS) reveals nitrogen contents of 5.39 and 5.10 atomic % in micro-FeCo-Nx-CN and meso/micro-FeCo-Nx-CN-30, respectively (Figure S7). The highresolution N 1s spectra of the catalysts show that addition of silica template did not significantly change the chemical structure of the material, since the ratio of different N species is similar in all FeCo-Nx-CN catalysts. The metal content in meso/micro-FeCo-Nx-CN is 0.52 atomic % (0.40 for iron, and 0.12 for cobalt), and in micro-FeCo-Nx-CN is 0.47 atomic % (0.33 for iron, and 0.14 for cobalt) (Figure S8). The high resolution XPS spectra of Fe and Co peaks (Figure S9) was fitted into only Fe<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, and Co<sup>3+</sup> for both samples of micro-FeCo-N<sub>x</sub>-CN and meso/micro-FeCo-N<sub>x</sub>-CN, no metallic Fe and Co was detected, which were consistent with the powder X-Ray Diffraction (XRD) results (Figure S10), thus indicating there are only atomic dispersion of Fe and Co active site in the Ndoped carbon matrix, also known as  $\mbox{Fe-}N_x$  and  $\mbox{Co-}N_x.^{[12]}$  The similar elemental component from XPS, indicates that the introducing of mesoporosity did not significantly change the chemical structure and composition of the materials.

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**Figure 3.** a) Schematic illustration of ORR and OER on meso/micro-FeCo-N<sub>x</sub>-CN. b) RDE polarization curves for micro-FeCo-N<sub>x</sub>-CN, meso/micro-FeCo-N<sub>x</sub>-CN, meso/micro-FeCo-N<sub>x</sub>-CN, and Pt/C catalysts for ORR. c) RDE polarization curves of micro-FeCo-N<sub>x</sub>-CN, meso/micro-FeCo-N<sub>x</sub>-CN, meso/micro-FeCo-N<sub>x</sub>-CN and Pt/C catalysts for OER. d) Corresponding Tafel plot of OER activity in c. e and f)  $E_{gap}$  difference of micro-FeCo-N<sub>x</sub>-CN and meso/micro-FeCo-N<sub>x</sub>-CN. Durability of the meso/micro-FeCo-N<sub>x</sub>-CN catalysts g) for ORR and f) for OER. h) Comparison of  $E_{gap}$  values for our catalysts with some current designed state-of-art bifunctional catalysts, these catalysts are cited from references 5-7.

It can be assumed that the meso/microporous structure found in the silica templated material will be beneficial for both gas and electrolyte diffusion during the electrochemical reaction (Figure 3a). Therefore, the catalytic performance of meso/micro-FeCo-N<sub>x</sub>-CN and micro-FeCo-N<sub>x</sub>-CN catalysts towards both ORR and OER were evaluated and compared using the rotating disk electrode (RDE) technique. The polarization curves for meso/micro-FeCo-N<sub>x</sub>-CN-30 catalysts for ORR (Figure 3b) show a high onset potential of 954 mV vs. RHE and half-wave potential of 886 mV vs. RHE, which are 54 mV and 58 mV higher for micro-FeCo-N<sub>x</sub>-CN. Furthermore, the limited current density for meso/micro-FeCo-Nx-CN-30 can reach to 6.3 mA/cm<sup>2</sup>, which is much higher than the one observed for micro-FeCo-N<sub>x</sub>-CN (5.3 mA/cm<sup>2</sup>) and even for a commercial Pt/C catalyst (5.6 mA/cm<sup>2</sup>). This high limited current density of meso/micro-FeCo-Nx-CN catalysts seem indeed a consequence of the hierarchically micro- and mesoporous structure, which facilitates gas diffusion and mass transfer. Indeed, also all other meso/micro-FeCo-N<sub>x</sub>-CN catalysts (Figure S8) synthesized with different ratio of silica template show higher onset potential, halfwave potential and limited current density than micro-FeCo-Nx-CN. The OER polarization curves in Figure 3c shows that the onset of meso/micro-FeCo-Nx-CN-30 (1.60 V) is lower than for micro-FeCo-N<sub>x</sub>-CN (1.63 V), also the potential at current density of 10 mA/cm<sup>2</sup> is 1.67 V for meso/micro-FeCo-N<sub>x</sub>-CN-30 and 1.71 V for micro-FeCo-Nx-CN. The corresponding Tafel plot of the

OER curve (Figure 3d) reveals a low Tafel slope of 57 mV/dec for meso/micro-FeCo-N<sub>x</sub>-CN-30 suggesting a good kinetic process (which indicates the natural activity of the catalytic active site). This remarkable ORR and OER bifunctional activity of meso/micro-FeCo-N<sub>x</sub>-CN gives an exceptional low  $E_{gap}$  of 0.78V between ORR half-wave potential and OER potential at a current density of 10 mA/cm<sup>2</sup> (Figure 3e). Figure 3f shows the  $E_{gap}$  is decreased from 0.88V to 0.78V owning to the introducing of mesoporosity. Meso/micro-FeCo-N<sub>x</sub>-CN-20 and -40 were also investigated for OER (Figure S9), which again reveal the enhanced activity by introducing mesoporosity, except for meso/micro-FeCo-N<sub>x</sub>-CN-40 in which the partial structural collapse seems to hinder fast gas diffusion.

To further reveal the influence of the different metal species on catalytic activity a comparable material but without Co addition (meso/micro-Fe-N<sub>x</sub>-CN-30) was synthesized and the activity of for both ORR and OER were compared. Although meso/micro-Fe-N<sub>x</sub>-CN-30 shows almost the same onset potential and half-wave potential for ORR with meso/micro-FeCo-N<sub>x</sub>-CN, a significant difference in OER reaction is observed by introducing Co. The OER potential at a current density of 10 mA/cm<sup>2</sup> for meso/micro-Fe-N<sub>x</sub>-CN is 1.71V, i.e. 0.04V higher than for meso/micro-FeCo-N<sub>x</sub>-CN. The Tafel plot of meso/micro-Fe-N<sub>x</sub>-CN shows a Tafel slope of 102 mV/dec which is again much higher than that for meso/micro-FeCo-N<sub>x</sub>-CN (57

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mV/dec) indicating is much slower kinetic process. It can thus be concluding that the activity of the FeCo-N<sub>x</sub> active sites is much higher than for a Fe-N<sub>x</sub> active site alone. Therefore, the stability of the meso/micro-FeCo-N<sub>x</sub>-CN-30 for both ORR and OER were measured by chronoamperometry scan (Figure 3g) and chronopotentiometry scan (Figure 3h). The current of ORR after 10 hours can maintain more than 95%. When keep working at current density of 10 mA/cm2 for OER, the potential can maintain under 1.7 V. These show good durability of

meso/micro-FeCo-N<sub>x</sub>-CN-30 for both ORR and OER during longtime work. Furthermore, we also summarized and compared the performances of some current designed state-of-art bifunctional catalysts with our meso/micro-FeCo-N<sub>x</sub>-30 catalyst in terms of the  $E_{gap}$  and the catalyst loading amounts (Figure 3h), more detailed data comparison was shown in Table S2. Based on these analysis, we can draw the conclusion that our catalyst shows outstanding reversible oxygen catalytic performances.



**Figure 4.** a) Open-circuit-potential of the Zn-air battery equipped with meso/micro-FeCo-Nx-CN-30 catalyst; b) cycle performance of Zn-air batteries with meso/micro-FeCo-Nx-CN-30 and Pt/C catalysts at a current density of 5 mA/cm<sup>2</sup> and then 10 mA/cm<sup>2</sup> (20 mins for each cycle); c) cycle performance of meso/micro-FeCo-Nx-CN-30 equipped battery at a current density of 20 mA/cm<sup>2</sup> for 20 hours; d) discharge curves of Zn-air batteries with meso/micro-FeCo-Nx-CN-30 equipped battery at a current density; e) long-time charge and discharge of the meso/micro-FeCo-Nx-CN-30 equipped battery at 10 mA/cm<sup>2</sup> (2 hours for each cycle).

A rechargeable liquid Zn-air battery was assembled to evaluate the activity of the bifunctional meso/micro-FeCo-Nx-CN catalysts for such devices (Figure S13). A Zn foil was used as anode and the catalyst-loaded carbon cloth with gas diffusion layer as cathode. 0.2 M Zn(OAc)<sub>2</sub> in 6.0 M aqueous KOH was used as electrolyte. As shown in Figure 4a, the open-circuitpotential of the Zn-air battery equipped with meso/micro-FeCo-Nx-CN is ~1.4 V. The discharge curves and corresponding power density of the Zn-air battery catalyzed by meso/micro-FeCo-N<sub>x</sub>-CN in comparison with Pt/C, suggesting the superior activity of meso/micro-FeCo-Nx-CN. The maximum power density of meso/micro-FeCo-Nx-CN battery is determined to be as high as 150 mW/cm<sup>2</sup>, three times higher than the power density of Pt/C. The rechargeability of the batteries were measured by charge and discharge cycles under different current density (Figure 4b and 4c). When charge-discharge cycling test at current density of 5 mA/cm<sup>2</sup> (Figure 4b) were carried out, the discharge voltage of the meso/micro-FeCo-Nx-CN equipped battery is about 1.26 V, 0.1 V higher than that of Pt/C equipped battery (1.16 V); the charge voltage is 2.01 V, even 0.5 V lower than that of Pt/C equipped battery (2.51 V).

When the cycling test is carried out more than 40 hours, the voltage of the meso/micro-FeCo-Nx-CN equipped battery is still quite stable, while Pt/C based battery shows a large voltage decrease in the discharge process and also large voltage increase during the charge process. The performance and stability of meso/micro-FeCo-Nx-CN equipped battery at higher charge-discharge current density was also detected, showing that the battery run stable for more than 20 hours under 20 mA/cm<sup>2</sup>, the charge-discharge voltage gap in this case was only ~0.91 V. An excellent cyclability of the battery can be observed even at long charge-discharge periods (2 hours), indicating the high application potential in rechargeable Zn-air battery. The above results highlight again the high ORR and OER catalytic activity and stability of the meso/micro-FeCo-Nx-CN catalysts, which can work robustly as bifunctional catalysts for advanced rechargeable Zn-air electrode and other related applications. The performance of our Zn-air battery is also compared with the currently reported results in Table S3 for detail. The superior electrochemical performances of meso/micro-FeCo-Nx-CN catalysts for both ORR and OER can be attributed to several factors: (1) the nanometer thickness of carbon sheets can

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efficiently enhance the transfer speed for both electrons and oxygen; (2) the combination of Fe, Co with N-doping can modulate the electronic properties and surface polarities, thus improving the activity of the catalyst; (3) the high specific surface area and balanced microporous and mesoporous structures make the active sites fully accessible and improve the transport properties of ORR/OER-relevant species.

In summary, we developed a facile strategy to synthesize meso/micro-FeCo-N<sub>x</sub>-CN as high performance reversible bifunctional oxygen catalysts in advanced rechargeable Zn-air batteries by parallel application of a salt and silica template. The materials exhibit with a well-defined 2D morphology, hierarchically meso- and microporous structure, homogenous dispersion of single metal-atoms or very small metal-clusters and enriched reversible oxygen electrocatalytic sites. These guarantee its structural features eventually excellent electrocatalytic performances both in ORR and OER, thus presenting great potential as efficient bifunctional oxygen electrode in next-generation rechargeable liquid Zn-air battery. This one-step synthetic route should make a facile and scalable production of differently designed heteroatom and metal-doped catalytic materials possible, giving a wide adaptability to current manufacturing processes and for a broad range of applications.

#### **Experimental Section**

Experimental details are shown in the supporting information.

#### Acknowledgements

This work was financially supported by the Cluster of Excellence Unifying Concepts in Catalysis (UniCat) and the Berlin Graduate School of Natural Sciences and Engineering (BIG-NSE), both funded by the German Science Foundation (DFG).

We are grateful to Anna Carlsson, Thermo Fisher Scientific for providing the HAADF-STEM measurements. We also thank Jan Ron Justin Simke and ZELMI TU-Berlin for the SEM and TEM measurements.

**Keywords:** active salt/silica-templating  $\cdot$  2D meso/microstructured carbon  $\cdot$  FeCo-N<sub>x</sub> heteroatoms doping  $\cdot$  reversible oxygen electrocatalyst  $\cdot$  rechargeable Zn-air battery

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## COMMUNICATION

An active salt/silica-templating approach for the facile synthesis of hierarchical meso/microporous Fe/Co-N<sub>x</sub>-doped carbon nanosheets is presented. These materials achieve high performance as bi-functional oxygen-electrodes. The resulting FeCo-N<sub>x</sub>-carbon reveals a welldefined 2D morphology and homogenous metal-atom doping, which yield enriched active sites for ORR-OER. These unique features lead to excellent and reversible oxygen electrocatalytic performance, which show its potential in rechargeable Zn-air battery.

10 meso/micro-FeCo-Nx-CN-30 micro-FeCo-Nx-CN H<sub>2</sub>O O 0 78 HO

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Active Salt/Silica-Templated 2D Mesoporous FeCo-Nx-Carbon as Bifunctional Oxygen-Electrodes for Zn-Air Batteries

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