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## Directed Growth of Metal-Organic Frameworks and Their Derived Carbon-Based Network for Efficient Electrocatalytic Oxygen Reduction

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The oxygen reduction reaction (ORR) is one of the heart processes of renewable-energy technologies including fuel cells and metal-air batteries.<sup>[1]</sup> Noble metal-based materials (e.g., Pt, Pd, and Au) have been widely used as the electrocatalysts toward ORR.<sup>[2]</sup> but the scarcity, high cost, and low stability of these noble metal-based catalysts hinder their practical applications. Alternatively, considerable attention has been paid to explore nonprecious metal catalysts, such as transition metalbased materials (e.g., oxides, chalcogenides, nitrides, and oxynitrides)<sup>[3]</sup> as well as carbon-based catalysts.<sup>[4]</sup> Among them, the heteroatom (e.g., N, B, P, Co, Fe)-doped carbons have been recognized as one of the most promising ORR catalysts due to their unique electronic properties and structural features.<sup>[5]</sup> For instance, the N-doped CNT<sup>[5a]</sup> and graphene<sup>[5b]</sup> show excellent activity for oxygen reduction attributed to the effective activation of carbon atoms by electronegative N. The key issue to obtain optimal ORR activities by using the doped carbon lies in a uniform doping of heteroatoms and a unique nanostructure with high surface area and suitable mesopore distribution. Great efforts have been focused on the preparation of doped carbon materials via several well-developed methods, e.g., the post-treatment of carbon materials with heteroatom substances (e.g., NH<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, or triphenylphosphine),<sup>[5e,6]</sup> or direct pyrolysis of the heteroatom-containing organic compounds under inert gas atmosphere.<sup>[5h,7]</sup> However, a sufficient doping and finecontrolled structure are rather difficult to be achieved simultaneously. Therefore, a uniform distribution of dopants into a well-designed carbon matrix with largely enhanced ORR performances remains a challenging goal.

Recently, it has been reported that metal-organic frameworks (MOFs) can be directly converted into various carbonbased functional materials via a pyrolysis process.<sup>[8]</sup> However, MOFs crystals are prone to aggregate into a bulk phase with the absence of porous structure, which largely reduces the resulting electrochemical performances.<sup>[8c]</sup> If an appropriate template is used as both a scaffold and a directing agent for the epitaxial growth of MOFs arrays, a subsequent pyrolysis process would



produce carbon-based materials with ordered stacking and porous nanostructure.<sup>[8c-f]</sup> This inspires us to refer to a 2D inorganic matrix, layered double hydroxides (LDHs), which consist of brucite-like [Mg(OH)<sub>2</sub>] host sheets with edge-sharing metal-O<sub>6</sub> octahedra (lateral particle size ranging from nanometer to micrometer-scale).<sup>[9]</sup> It has been reported that the surface metal cations of LDHs exist at an unsaturated coordination state,<sup>[10]</sup> enabling them as active sites for the in situ nucleation and directed epitaxial growth of MOFs.

Herein, we report the design and fabrication of a well-defined carbon-based architecture by in situ nucleation and directed growth of MOFs arrays on the surface of LDHs nanoplatelets, followed by a subsequent pyrolysis process, which exhibits largely enhanced electrocatalytic ORR performances. The asprepared MOFs arrays are strongly and uniformly anchored onto the surface of LDHs scaffold, which ensures the structural transformation from MOFs to carbon-based arrays with fine control over composition and morphology. The resulting 2D carbon-based network shows desirable features, including highly effective active sites (e.g., N-C, Co-N-C), a surface area of 220 m<sup>2</sup> g<sup>-1</sup> and hierarchical micro-/mesoporous structure (mainly centered at 1.5-3 nm and 10-20 nm). Consequently, this electrocatalyst exhibits excellent ORR activity and stability (an onset potential of 0.94 V versus RHE and ≈99% current retention over 20000 s), which is superior to the commercial Pt/C material.

The preparation process is illustrated in Figure 1a, which involves the directed growth of zeolitic imidazolate framework (ZIF-67) on the surface of CoAl-LDH nanoplatelets (denoted as CoAl-LDH@ZIF-67) followed by a subsequent pyrolysis treatment to achieve a porous carbon-based framework (see the Supporting Information for details). The sandwich-like CoAl-LDH@ZIF-67 composite material was first prepared through in situ precipitation of ZIF-67 on the surface of CoAl-LDH nanoplatelets by immersing CoAl-LDH into a solution containing cobalt nitrate and 2-methylimidazole (MeIM) at room temperature. After reaction for 15 min, ZIF-67 crystals with a diameter of  $\approx 200$  nm were uniformly coated on the both sides of CoAl-LDH nanoplatelet, accompanied with the sample color change from pink to purple (Figure 1b,c). Then, the as-obtained CoAl-LDH@ZIF-67 was further pyrolyzed in a temperature-programmed furnace under nitrogen gas flow at 800 °C for 2 h (the resulting product is denoted as LDH@ZIF-67-800). In order to give a thorough comparison study, two control samples are provided: ZIF-67 and ZIF-67-R, prepared via the benign conditions in this work (room

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**Figure 1.** a) Schematic illustration for the synthesis of porous honeycomb-like carbon-based framework. SEM images of b) CoAl-LDH, c) CoAl-LDH@ ZIF-67, and d) LDH@ZIF-67-800. e,f) STEM images of LDH@ZIF-67-800. g) HRTEM image and h) corresponding SAED pattern of LDH@ZIF-67-800. i) The low magnification HRTEM image and j) corresponding particle size distribution of the Co nanoparticles for LDH@ZIF-67-800.

temperature, 15 min) and via the previously reported synthesis conditions (120 °C, 12 h),<sup>[8j]</sup> respectively. Their derived carbon materials are denoted as ZIF-67-800 and ZIF-67-800-R accordingly. SEM images of LDH@ZIF-67-800 display a typical 2D porous structure with continuous honeycomb holes anchoring to both sides of the nanoplatelet (Figure 1d; Figure S1, Supporting Information). A slight shrink in the thickness of LDH@ZIF-67 is observed from ≈600 to ≈500 nm after pyrolysis owning to the partial collapse of the original ZIF-67. Scanning transmission electron microscopy (STEM) images further confirm this 2D porous morphology of LDH@ ZIF-67-800 with a lateral particle size of  $\approx 6 \ \mu m$ , close to the size of CoAl-LDH template (Figure 1e,f). The detailed nanostructure of LDH@ZIF-67-800 is investigated by high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED). Graphite-like layers can be easily identified at the pore wall with an interlayer spacing of 0.334 nm (Figure 1g), corresponding to the (002) plane of graphitic carbon.<sup>[11a]</sup> The HRTEM image combined with SAED pattern shows that the Co nanoparticles with well-resolved (111) lattice fringe of 0.204 nm are encapsulated in a highly graphitic carbon shell (Figure 1g,h).<sup>[11b]</sup> In addition, the Co nanoparticles are well dispersed with a narrow particle size mainly centered

at 11 nm in diameter (Figure 1i,j; Figure S2, Supporting Information). The results above indicate that the pyrolysis process induces two structural changes: the ZIF-67 shell transforms to porous graphitic carbon while the LDHs nanoplatelet core turns to Co nanoparticles. In contrast, the pyrolysis of pristine ZIF-67 crystals only gives agglomerated carbon-based particles without porous nanostructure (Figure S3, Supporting Information).

Figure 2a shows the X-ray diffraction (XRD) patterns of CoAl-LDH, ZIF-67, CoAl-LDH@ZIF-67, and their derived pyrolysis products (denoted as CoAl-LDH-800, ZIF-67-800 and LDH@ZIF-67-800, respectively). The XRD pattern of CoAl-LDH@ZIF-67 displays a superimposition of LDH phase<sup>[9d]</sup> and ZIF-67 phase,<sup>[8b]</sup> indicating the effective combination of LDH and ZIF-67. After pyrolysis, the original peaks are replaced by a series of new reflections at  $\approx 26^{\circ}$ , 44° and 51°, which correspond to the (111) and (200) crystal planes of face-centeredcubic (fcc) Co phase and the (002) diffraction peak of graphitic carbon, respectively.[11b] This is consistent with the results of HRTEM image (Figure 1g). Raman spectrum provides further evidences for the formation of graphitized carbon: the G band at 1590 cm<sup>-1</sup> and D band at 1330 cm<sup>-1</sup> are clearly resolved (Figure S4, Supporting Information). It is worth mention that no cobalt oxide or cobalt-aluminum spinel phase is found in

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Figure 2. a) XRD patterns of CoAl-LDH, ZIF-67, CoAl-LDH@ZIF-67 and their derived pyrolysis products. b) XPS spectra of CoAl-LDH-800, ZIF-67-800, and LDH@ZIF-67-800. c)  $N_2$  sorption isotherms of CoAl-LDH-800, ZIF-67-800, and LDH@ZIF-67-800 (inset shows the pore size distribution).

LDH@ZIF-67-800 sample owing to the reduction of  $\mathrm{Co}^{2+}$  to metallic Co by carbon.<sup>[12]</sup> The full XPS spectrum of LDH@ZIF-67-800 reveals signals of C, N, O, and Co element (Figure 2b). Among them, the high resolution Co 2p XPS spectrum shows three types of Co species, namely, metallic Co (778.5 eV), CoO<sub>x</sub> or  $CoC_xN_v$  (780.5 eV) and Co-N<sub>v</sub> (782 eV) with a content of 49.3%, 28.2% and 22.5%, respectively (Figure S5, Supporting Information). The results verify the presence of Co-N bond, which has been demonstrated as one of the most efficient active sites for ORR.<sup>[8b]</sup> In addition, elemental contents of C, N, O, and Co of LDH@ZIF-67-800 are further measured by EDX spectra (Figure S6, Supporting Information), which give 87.16%, 4.81%, 5.62%, and 2.36% for C, N, O, and Co, respectively, approximately consistent with the results of XPS analysis (Table S4, Supporting Information). The surface area and poresize distribution are further investigated by N2-adsorption/desorption measurements. A type-IV isotherm with sharp uptakes at low relative pressure (<0.05) and H3-type hysteresis loops (uptakes at a relative pressure ranging from 0.45 to 1.0) are observed for the sample of LDH@ZIF-67-800, indicating the coexistence of micropore and mesopore (Figure 2c).<sup>[8f,9d]</sup> Poresize distributions (mainly centered at 1.5-3 nm and 10-20 nm) obtained from the adsorption isotherm further confirm its hierarchical micro-/mesoporous structure (Figure 2c, inset); while the ZIF-67-800 and CoAl-LDH-800 sample show much limited mesopores. Moreover, the maximum specific surface area is also presented in the sample of LDH@ZIF-67-800 (220 m<sup>2</sup> g<sup>-1</sup>), significantly larger than that of ZIF-67-800 (47 m<sup>2</sup> g<sup>-1</sup>) and

CoAl-LDH-800 (9 m<sup>2</sup> g<sup>-1</sup>). It is worth mention that the specific surface area of ZIF-67-800-R (275 m<sup>2</sup> g<sup>-1</sup>) is much larger than that of ZIF-67-800 (47 m<sup>2</sup> g<sup>-1</sup>) in this work (Figure S7, Supporting Information), owing to the significantly different aging conditions for the ZIF-67 precursor (the former: 120 °C, 12 h; the latter: room temperature, 15 min).

The key role of CoAl-LDH to the directed growth of MOFs was further studied. It is found that the color of CoAl-LDH suspension turns from pink to purple after mixing with MeIM solution (Figure S8a, Supporting Information), but no color change occurs in the case of MgAl-LDH/MeIM (Figure S8b, Supporting Information) and no well-organized carbon architecture is observed after the following pyrolysis process (Figure S9, Supporting Information). This indicates a specific metal-imidazole interaction between Co cation in the CoAl-LDH and MeIM. Further experiments show that the atom density of Co in the CoAl-LDH layer imposes great influences on the growth of MOFs and the resulting carbon-based nanostructure. As shown in Figure 3a,e,i, by using AlOOH nanoplatelet as a template, ZIF-67 nanocrystals are absorbed on its surface, but a hierarchical carbon-based structure cannot be obtained. After introducing a low content of Co into AlOOH (Co/Al molar ratio = 1:2), sparse ZIF-67 nanocrystals grow on the LDH surface and thin carbon caves are observed via the pyrolysis process (Figure 3b,f,j; Figure S10, Supporting Information). With the increase of Co/Al molar ratio to 2:1 (Figure 3c), ZIF-67 crystals grafting on the CoAl-LDH nanoflakes become more densely with an uniform orientation (Figure 3g), which convert





**Figure 3.** Structure model of a) AlOOH nanoplatelet, CoAl-LDH with various Co/Al molar ratios: b) 1:2, c) 2:1, d) Co(OH)<sub>2</sub> nanoplatelet. SEM images of e) AlOOH@ZIF-67, f) CoAl-LDH@ZIF-67 (Co/Al ratio = 1:2), g) CoAl-LDH@ZIF-67 (Co/Al ratio = 2:1), h) Co(OH)<sub>2</sub>@ZIF-67, and their corresponding pyrolysis products i–l).

to a well-organized 2D honeycomb-like carbon framework (Figure 3k). However, a further enhancement of Co content results in a serious aggregation of ZIF-67 and the damage of honeycomb carbon structure (Figure S11, Supporting Information). Moreover, ZIF-67 supported on a pristine Co(OH)<sub>2</sub> nanoplatelet does not produce an ordered carbon nanostructure (Figure 3d,h,l). In addition, the replacement of ZIF-67 by ZIF-8 (the connectors are substituted by Zn<sup>[8a]</sup>) also fails to induce the formation of honeycomb-like carbon after pyrolysis at 800 °C (Figure S12, Supporting Information). As demonstrated above, the highly dispersed Co element in the lamellar CoAl-LDH acts as efficient active sites for the in situ nucleation and directed growth of ZIF-67 nanocrystals. Subsequently, a pyrolysis treatment of the highly-oriented ZIF-67 arrays results in the welldefined and porous carbon-based network, which inherits the structure characteristics of the precursor. The optimum preparation conditions for CoAl-LDH@ZIF-67 were further explored: a 15 min of synthetic time with precursor concentration of 0.8 M MeIM + 0.1 M Co<sup>2+</sup> (see Figures S13-S15, Supporting Information).

To learn the structural evolution during pyrolysis process, CoAl-LDH@ZIF-67 pyrolyzed at different temperatures was investigated. TGA curve (Figure S16, Supporting Information) shows that the organic framework starts to collapse at  $\approx$ 310 °C with a continuous weight loss until  $\approx$ 570 °C. Above 570 °C, both the reduction of cobalt ions and the construction of graphitized carbon occur, which can be confirmed by XRD and Raman spectrum. As shown in the XRD patterns of CoAl-LDH@ZIF-67 from 600 to 900 °C, the (111) and (200) reflection of Co phase appear with increasingly strengthened intensity, indicating the reduction of Co (Figure S17, Supporting Information). During the same pyrolysis process, the intensity

ratio of the D band to G band  $(I_D/I_G)$  in the Raman spectrum (Figure S18, Supporting Information) decreases from 1.45 to 1.06, further verifying the formation of graphitized carbon.<sup>[7e]</sup> SEM images display that the ZIF-67 nanocrystals grafting on the surface of CoAl-LDH collapse gradually from 150 to 600 °C, due to the dehydration and carbonization of organic linkers (Figure S19a–e, Supporting Information). As the pyrolysis temperature rises to 800 °C, a well-defined honeycomb-like morphology on the LDH nanoflake is observed (Figure S19f, Supporting Information), which inherits the structure characteristics of the highly-oriented ZIF-67 precursor. However, this structure is seriously destroyed when the temperature is higher than 800 °C (Figure S19g, Supporting Information).

The ORR catalytic activities of LDH@ZIF-67-800 and corresponding reference samples in alkaline solution (0.1 M KOH) are investigated by cyclic voltammetry (CV), rotating disk electrode (RDE), and rotation ring-disk electrode (RRDE), respectively. As shown in Figure 4a, the obviously enhanced cathodic peak for LDH@ZIF-67-800 in O2-saturated solution compared with that in N2-saturated electrolyte implies a significant ORR activity of this sample. The ORR performance of the as-prepared catalysts was further studied by Linear Sweep Voltammetry (LSV). As shown in Figure 4b and Figure S20 (Supporting Information), LDH@ZIF-67-800 exhibits a more positive onset potential (0.94 V vs RHE) and half-wave potential (0.83 V vs RHE) as well as larger diffusion-limited current density (5.5 mA cm<sup>-2</sup>), superior to the performances of CoAl-LDH-800, ZIF-67-800, and ZIF-67-800-R (see Table S1 for detailed results in the Supporting Information). Moreover, LDH@ZIF-67-800 also shows enhanced ORR activity in comparison with commercial Pt/C (20%) catalyst (see Figure S21 for detailed characterizations in the Supporting Information). RDE measurements at various

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**Figure 4.** a) CV curves of LDH@ZIF-67-800 in N<sub>2</sub> and O<sub>2</sub>-saturated solution, respectively. b) Linear sweep voltammetry (LSV) curves of CoAl-LDH-800, ZIF-67-800, LDH@ZIF-67-800, and Pt/C catalyst in 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. c) LSV curves for LDH@ZIF-67-800 at various rotation rates. d) Corresponding Kouteck–Levich plots derived from the RDE data. e) Tafel slope values of low and high overpotential regions for LDH@ZIF-67-800, ZIF-67-800, and Pt/C catalyst at various potentials based on the RRDE data.

rotating speeds at a scan rate of 10 mV s<sup>-1</sup> in an O<sub>2</sub>-saturated system are carried out and the Koutecky–Levich (K-L) equation is used to analyze the kinetic parameters (Figure 4c). The linearity of K-L plots for LDH@ZIF-67-800 indicates a first-order reaction kinetics with regard to the similar electron transfer numbers (*n*) at various potentials (Figure 4d).<sup>[8f]</sup> The calculated results reveal an electron transfer number of ≈4.0 within 0.2–0.7 V versus.RHE for LDH@ZIF-67-800, indicating a direct four electron oxygen reduction process. This electron transfer number is close to that of Pt/C catalyst (Figure S22, Supporting Information) and much larger than that of other reference catalysts (as shown in Figure S23–S24 and Table S2 in the Supporting Information), further demonstrating a higher activity of

LDH@ZIF-67-800. This can be attributed to the unique hierarchical micro-/mesoporous structure that benefits the fast diffusion of  $O_2$  and electrolyte during the ORR process.

To analyze the kinetic properties of ORR by using the prepared electrocatalysts, the Tafel slopes were obtained from the linear plots of LSVs at 1600 rpm (Figure 4e; Figure S25, Supporting Information). All of these plots show typical two-stage linear regions at low overpotential ( $\eta_L$ ; where the overall ORR speed is determined by the surface reaction rate on the catalyst) and high overpotential ( $\eta_H$ ; where the overall ORR rate is dependent on the oxygen diffusion).<sup>[13,4b]</sup> Both the Tafel slopes at  $\eta_L$  (63 mV dec<sup>-1</sup>) and  $\eta_H$  (115 mV dec<sup>-1</sup>) for the LDH@ZIF-67-800 are much lower than those of the





commercial Pt/C catalyst (72 mV dec<sup>-1</sup> at  $\eta_L$ ; 132 mV dec<sup>-1</sup> at  $\eta_H$ ) and pristine ZIF-67 derived carbon (67 mV dec<sup>-1</sup> at  $\eta_L$ ; 125 mV dec<sup>-1</sup> at  $\eta_H$ ), suggesting that the LDH@ZIF-67-800 possesses a faster electron transfer rate and a more efficient reactant diffusion. To further quantify the ORR pathway, a rotation ring-disk electrode (RRDE) technique is conducted to monitor the formation of HO<sub>2</sub><sup>-</sup> during the ORR process (Figure S26, Supporting Information). As shown in Figure 4f, the HO<sub>2</sub><sup>-</sup> yield of LDH@ZIF-67-800 is below 10% and the electron transfer number (*n*) ranges in 3.86–3.98, close to that of Pt/C and consistent with the results obtained from the K-L plots based on the RDE study. The LDH@ZIF-67-800 catalyst also shows a good ORR activity in acidic solution (0.1  $\bowtie$  HClO<sub>4</sub>).

As shown in Figure S27 and S28 (Supporting Information), the LDH@ZIF-67-800 catalyst exhibits an onset potential of 0.875 V versus RHE, half-wave potential of 0.675 V versus RHE and diffusion-limited current density of 5.1 mA cm<sup>-2</sup> at 0.1 V versus RHE, much close to those of Pt/C catalyst. Moreover, the HO<sub>2</sub><sup>-</sup> yield of LDH@ZIF-67-800 in acidic solution is below 10% and the electron transfer number (*n*) ranges in 3.85–3.96, also close to Pt/C and consistent with the results obtained from the K-L plots based on the RDE study. It is worth mention that the LDH@ZIF-67-800 exhibits clear advantages compared with other MOFs derived ORR catalysts reported so far (e.g., P-Z8-Te-1000, FeIM/ZIF-8, ZIF-67-900, etc.); the corresponding comparisons are given in Table S3 (Supporting Information).



**Figure 5.** a) SEM and b) HRTEM images of the LDH@ZIF-67-800 sample after acid leaching (NPC-800). c) High-resolution XPS N1s spectra of LDH@ ZIF-67-T (T = 600, 700, 800, and 900 °C, respectively). d) Percentage of various nitrogen species as a function of pyrolysis temperature. e) Linear sweep voltammetry (LSV) curves of NPC-800 and LDH@ZIF-67-T (T = 600, 700, 800, and 900 °C) in O<sub>2</sub>-saturated 0.1 M KOH at a sweep rate of 10 mV s<sup>-1</sup> and electrode rotation speed of 1600 rpm.

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Figure 6. a) Current-time (I-t) curves for LDH@ZIF-67-800 and Pt/C in O2-saturated 0.1 M KOH solution without and with 2 M MeOH. b) I-t curves for LDH@ZIF-67-800 and Pt/C in O<sub>2</sub>-saturated 0.1 м solution KOH at 0.5 V versus RHE and 1600 rpm.

Previous studies have shown that both the types of nitrogen species and encapsulated metal particles play a crucial role in the performance of pyrolyzed carbonbased ORR electrocatalysts.<sup>[8b-f]</sup> To verify the active sites of obtained carbon-based network, the metal Co nanoparticles in LDH@ZIF-67-800 was first removed by 10 wt% HF solution (denoted as NPC-800).<sup>[14]</sup> Although the sample of NPC-800 exhibits a well-kept honeycomb-like morphology (Figure 5a), the embedded Co nanoparticles have been successfully removed which is confirmed by HRTEM image (Figure 5b), XRD pattern and magnetism test (Figure S29, Supporting Information). As demonstrated by the LSV measurements, the NPC-800 sample gives an inferior ORR performance compared with LDH@ZIF-67-800, including a 5 mV decrease in onset potential, 12 mV decrease in half-wave potential, and 10% loss in diffusion-limited current density at 0.6 V versus RHE (Figure 5e; Figure S30, Supporting Information). Furthermore, LDH@ZIF-67-800 shows a less tafel slope (Figure S31a, Supporting Information) and a decreased charge transfer resistance (Figure S31b, Supporting Information) than those of NPC-800. The results above indicate that the presence of Co nanoparticles gives a positive contribution to the ORR performance of LDH@ZIF-67-800, which could be ascribed to the modified electron structure of the surrounding graphitic shell.<sup>[8d]</sup> We further employed XPS to investigate the role of doped-N at different pyrolysis temperatures (denoted as LDH@ZIF-67-T; T is the temperature). A remarkable reduction of N1s is observed with the increase of temperature, which is due to the loss of unstable nitrogen (Figure S32 and Table S4, Supporting Information).<sup>[8b,11b]</sup> The N1s peak is further deconvoluted into three different types of nitrogen species: pyridinic N (N1, 398.3 eV), pyrrolic N (N2, 400.1 eV), and graphitic N (N3, 401.0 eV) (Figure 5c). Both the N1 and N3 were reported to play a crucial role in the ORR process while the contribution of N2 is uncertain.  $\ensuremath{^{[8e]}}$  As the pyrolysis temperature rises, the relative composition of N1 and N2 species reduces gradually, while that of N3 increases significantly (Figure 5d). The composition of N1+N3 shows an increase along with the enhanced temperature to a maximum of ≈78.6% at 800 °C (Figure 5d; Table S5, Supporting

Information), which is in agreement with the trend of ORR activity of LDH@ZIF-67-T samples (T = 600, 700, 800, and900 °C, respectively). Both the onset potential and current density of LDH@ZIF-67-T improve gradually with the increase of pyrolysis temperature, which reach the optimized values at 800 °C (the onset potential decreases 70 mV; the current density increases 57% at 0.6 V versus RHE from 600 to 800 °C). This indicates that pyridinic N and graphitic N are more responsible for the ORR activity, consistent with the previous reports. However, the LDH@ZIF-67-900 shows an obvious degradation of the ORR performance, which might be attributed to the sharp loss of pyridinic N and the collapse of the honeycomb-like structure (Figure S19g, Supporting Information).

In addition to the activity, the stability is another key parameter for high-performance ORR catalysts, from the viewpoint of practical applications. In this work, chronoamperometric (CA) measurement was used to test the possible crossover effect caused by small organic molecules (e.g., methanol) for LDH@ZIF-67-800. As shown in Figure 6a, when 2 M methanol is added into the O<sub>2</sub>-saturated 0.1 M KOH electrolyte, no obvious performance decay is observed for LDH@ZIF-67-800. In contrast, the Pt/C catalyst shows a sharp decrease in current density, suggesting LDH@ZIF-67-800 exhibits a strong tolerance against chemical corrosion. Furthermore, the long-term stability of LDH@ZIF-67-800 was also confirmed by CA measurements. As shown in Figure 6b, LDH@ZIF-67-800 displays a superior durability with 99% retention over 20000 s of continuous operation, whereas Pt/C suffers from a faster current loss (only 60% retention), further demonstrating a superb longterm stability of the LDH@ZIF-67-800 catalyst toward ORR.

In summary, we have developed a facile and effective synthesis approach to prepare carbon-based network with finely controlled morphology and well-distributed hierarchical micro-/ mesoporous structure via a directed growth of MOFs arrays followed by a subsequent pyrolysis process. By tuning the Co density in the LDH layer, the 2D carbon-based framework with honeycomb-like morphology, hierarchical nanostructure, and uniform heteroatom doping (N, Co) has been successfully obtained. The resulting LDH@ZIF-67-800 material exhibits



promising ORR activity, which is superior to the Pt/C catalyst and among the highest reported performances of carbon-based electrocatalysts. In addition, the extraordinary long-term stability and excellent tolerance against methanol corrosion would guarantee its practical applications. By virtue of the versatility of LDHs and MOFs, the synthesis strategy presented here can be extended to the preparation of other LDHs/MOFs derived functional materials toward energy storage and conversion.

## **Supporting Information**

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

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