Metal-organic framework derived nitrogen-doped porous carbon@graphene sandwich-like structured composites as bifunctional electrocatalysts for oxygen reduction and evolution reactions

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Abstract

In this work, we have successfully prepared sandwich-like structured N-doped porous carbon@graphene composites (N-PC@G) derived from sandwich-like structured zeolitic imidazolate framework@graphene oxide (ZIF-8@GO). ZIF-8@GO was obtained by *in situ* controllable growth of ZIF-8 nanocrystals on both surfaces of graphene oxide (GO) sheets with different contents. Experimental results demonstrate that N-PC@G-0.02 (representing GO amount of 0.02 g in reaction precursors) **obtained at 900 °C** possesses high surface area (1094.3 m² g⁻¹), bimodal-pore structure (micropores and mesopores) and high graphitization degree, exhibiting great

potential as a bifunctional electrocatalyst for both ORR and OER. Compared to commercial Pt/C catalyst, the N-PC@G-0.02 shows superior electrocatalytic activity with onset and half-wave potentials of 1.01 V and 0.80 V (vs. RHE), respectively, better durability and high resistance to methanol crossover effect toward ORR in alkaline media. Also, the metal-free N-PC@G-0.02 also exhibits high electrocatalytic activity of OER, comparable to commercial RuO₂ catalyst. The superior ORR and OER performance could be due to a synergistic effect between ZIF-8 derived porous carbon and graphene with regard to structure and composition of N-PC@G-0.02 with high surface area, porous structure, and suitable N doping level and type, boosting the catalytic active sites, mass transport and electron transfer.

1. Introduction

Heteroatom doped/co-doped (*e.g.*, N, S, B, P) carbon-based materials with unique electronic properties and superior conductivity have been intensively investigated as promising electrocatalysts to replace expensive and scarce Pt-based materials for the applications in renewable energy technologies, such as fuel cells, metal-air batteries and water splitting to generate hydrogen and oxygen [1-5]. Among all synthetic strategies investigated to date, metal-organic frameworks (MOFs) constructed by metal/metal clusters (*e.g.*, Zn, Fe, Co *etc.*) and N-contained organic ligands have been recently a class of ideal precursors to prepare N-doped porous carbon-based materials for various applications, especially for electrocatalytic oxygen reduction reaction (ORR) and/or oxygen evolution reaction (OER) [6-9]. The outstanding application performance of MOFs based materials in different areas can be attributed to this kind

of materials possessing many unique features, such as high surface area, diverse composition, well-organized frameworks, controllable porous structure, size and shape at nanometer scale, and providing heteroatom doping source (*e.g.*, N) [10-12]. As pyrolysis precursors, MOFs materials with these advantages aforementioned can be readily transformed into corresponding carbon-based materials with high surface area, porous structure, superior conductivity and heteroatom doping (*e.g.*, N). These properties of MOFs derived carbon materials are critically important for high performance electrocatalysis applications [13-15]. Currently, MOFs derived carbon-based materials are used as high performance electrocatalysts for ORR and OER applications mainly in two forms, namely, the obtained porous carbon materials with and without metal species. Some studies have demonstrated that the presence of metal atoms (*e.g.*, Fe, Co *etc.*) in carbon structure derived from MOFs cannot only improve carbon graphitization degree to enhance electrical conductivity, importantly also provide more valid catalytic active sites by forming Fe(Co)-N_x moieties in carbon structure, thus increasing ORR and/or OER performance [16-18]. However, an opposite opinion addressed by other studies reveals that the involvement of metal atoms in carbon structure may be unsuitable for ORR and/or OER because strong basic media used for ORR and/or OER may result in metal leaching from carbon structure over time, thus losing the electrocatalytic activity and shelf life [11, 19]. Although the opinions mentioned above are still under debate, both forms of carbon-based catalysts derived from MOFs exhibit superior electrocatalytic activity toward ORR and/or OER [20-22].

Recently, zeolitic imidazolate frameworks (ZIFs) have been intensively investigated as pyrolysis precursors to fabricate N-doped porous carbon materials with large surface area and high N doping level [6, 7, 11, 23-25]. These ZIFs derived N-doped porous carbon materials by high temperature pyrolysis as electrocatalysts have demonstrated superior electrocatalytic activity toward ORR [11, 23, 25]. Many studies have indicated that the metal species such as Zn, Co not only act as metal skeletons to form ZIFs nanocrystals with organic ligands, also play an important role as a hard template in pyrolytic carbon structure, favorable for creating highly porous structures after the removal of metal species by acid or alkali etching [11]. This highly porous structure of the ZIFs derived carbon material can effectively facilitate mass transport, enabling full utilization of material pore inner catalytic active sites and thus significantly improving ORR performance [6, 11, 26]. Although ZIFs derived N-doped porous carbon as electrocatalyst possesses many advantages beneficial for high efficiency ORR, ZIFs nanocrystals directly derived carbon materials by high temperature pyrolysis inevitably generate drastic structural/morphological damage (*e.g.*, forming discrete carbon particles and low graphitization degree *etc.*), thus resulting in poor electrical conductivity and a great loss of catalytic active sites [7, 8]. All of these are unfavorable for high efficiency electrocatalysis applications (*e.g.*, ORR). To overcome this issue, some recent studies have demonstrated that ZIFs (*e.g.*, ZIF-8) nanocrystals can be *in situ* grown onto both surfaces of graphene oxide (GO) sheets in a controlled manner to form a sandwich-like structured ZIFs@GO composite [8, 16, 27]. Such sandwich-like structured composite can be readily converted into

N-doped porous carbon@graphene composite by high temperature pyrolysis, exhibiting significantly improved ORR catalytic activity when used as electrocatalyst [17, 27]. The high ORR performance can be ascribed to the N-doped porous carbon@graphene composite with many advantages [7, 8]: (1) superior electrical conductivity owing to a close contact between porous carbon structure and graphene to obtain a consecutive conductive network; (2) a synergistic effect between N-doped porous carbon and N-doped graphene to generate more catalytic active sites; (3) the formation of uniform porous structure due to *in situ* controllable growth of ZIFs nanocrystals onto GO sheets to minimize porous structure damage of ZIFs during high temperature pyrolysis. To date, metal-free N-doped porous carbon materials derived from ZIFs (*e.g.*, ZIF-8) by high temperature pyrolysis are exclusively used as electrocatalysts for ORR [7, 11, 25], almost few reports demonstrate ZIFs derived metal-free N-doped porous carbon materials as electrocatalysts for multifunctional electrocatalysis applications (*e.g.*, for **both** ORR and OER). Very recently, several studies reveal that metal-free heteroatom-doped/co-doped (*e.g.*, N, P) carbon materials (*e.g.*, porous carbon foam, graphene/single-wall carbon nanotube) can be used as bifunctional electrocatalysts for high performance ORR and OER applications [2, 28-30]. These studies give us great encouragement to develop high-performance and metal-free heteroatom (*e.g.*, N) doped carbon materials derived from MOFs nanocrystals as bifunctional electrocatalysts for **bifunctional** ORR and OER.

Herein, a sandwich-like structured N-doped porous carbon@graphene (N-PC@G) composite has been successfully fabricated by simple pyrolysis of zeolitic imidazolate

framework (ZIF-8)@graphene oxide (denoted as ZIF-8@GO) composite obtained by *in situ* controllable growth of ZIF-8 nanocrystals on both surfaces of GO sheets, followed by etching away metallic zinc (see Fig. 1). The resulting N-PC@G as electrocatalyst exhibits bifunctional electrocatalytic activity toward oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) (Fig. 1). For ORR application, the N-PC@G-0.02 (representing GO amount of 0.02 g in reaction precursors) obtained at 900 °C shows superior catalytic activity with more positive onset potential, good durability and high resistance to methanol crossover effect, comparable to or better than commercial Pt/C catalyst, while as OER catalyst the N-PC@G-0.02 demonstrates significantly higher catalytic activity than commercial Pt/C catalyst and comparable catalytic activity to commercial RuO₂ catalyst. The high ORR and OER performance of N-PC@G-0.02 could be due to a synergistic effect between N-doped porous carbon and N-doped graphene creating more catalytic active sites combining with its high surface area (1094.3 m² g⁻¹) favourable for the exposure of catalytic active sites, porous structure (mesopore and micropore) to improve mass transport, and high graphitization degree beneficial for electron transfer.

Fig. 1 Schematic illustration of a synthetic process of sandwich-like structured N-doped porous carbon@graphene (N-PC@G).

2. Experimental

2.1 Chemicals

Graphite powders (325 mesh, Alfa Aesar, 99.8%), 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, 98%, Aladdin Reagent), potassium hydroxide (KOH, 98%, Aladdin Reagent), and Nafion solution (5%, DuPont). Sulfuric acid, potassium permanganate, sodium nitrate, hydrogen peroxide (H_2O_2 , 30%) zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, $\geq 99.7\%$), hydrochloric acid (HCl 36%~38%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Commercial E-TEK Pt/C and RuO_2 catalysts were purchased from Alfa Aesar and Sigma-Aldrich, respectively. All the chemicals were used as purchased without any further purification.

2.2 Synthesis of N-PC@G-X

Fabrication of graphene oxide (GO): Graphene oxide was prepared by a modified Hummer method [31]. In a typical synthesis, 1.0 g graphite powders and 0.5 g NaNO_3 were added to 23 mL of concentrated H_2SO_4 (98%) under stirring in an ice bath. 6.0 g KMnO_4 was slowly added to the above mixture under stirring for 1 h at below 5 °C. Then the reaction was heated to 35 °C for 2 h under stirring. Subsequently, 46 mL of deionized water was slowly added into the above mixture under stirring at 98 °C for more than 15 min. The obtained suspension was further diluted with 140 mL of water and then 10 mL of H_2O_2 was injected into the above solution, the color of the solution changed from dark brown to bright yellow. The resulting mixture was washed adequately by HCl and deionized water for several times to obtain graphite oxide. As-prepared graphite oxide was further dispersed in water by ultrasonication treatment for 1 h to get rid of any aggregated nanosheets, and finally the suspension was centrifugated to obtain graphene oxide (GO) by further freeze drying treatment.

Fabrication of N-doped porous carbon@graphene (N-PC@G) composites: In a typical synthesis, GO with different amounts (0.02 g, 0.05 g and 0.1 g) was firstly dispersed ultrasonically in 20 mL of deionized water for 30 min, then 23 g 2-methylimidazole was added to the above GO aqueous solution under stirring to form a mixture. Subsequently, 20 mL of $\text{Zn}(\text{NO}_3)_2$ (0.12 M) aqueous solution was added into the above mixture under stirring at room temperature for 30 min. The product (ZIF-8@GO) was collected by centrifugation and washing with deionized water. After freeze drying, the obtained gray powder was pyrolyzed at 900 °C for 5 h

at a heating rate of 5 °C min⁻¹ under N₂ atmosphere. The pyrolytic product was subsequently immersed in 2.0 M HCl for overnight to remove zinc or other impurities, then N-doped porous carbon@graphene composite was obtained by further freeze drying (denoted as N-PC@G-X, X represents GO amount in reaction precursors). N-doped porous carbon (N-PC) was synthesized by direct pyrolysis of ZIF-8 without addition of GO at 900 °C for 5 h at a heating rate of 5 °C min⁻¹ under N₂ atmosphere; N-doped graphene (N-G) was obtained by pyrolyzing 100 mg GO and 1.0 g ZIF-8 which were separately placed in two different quartz boats next to each other at 900 °C for 5 h at a heating rate of 5 °C min⁻¹ under N₂ atmosphere.

2.3 Characterizations

Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Philips X-Pert Pro X-ray diffractometer with Cu-K α radiation (1.5418Å). Field emission scanning electron microscopy (FESEM) images of the samples were taken on a FESEM (Quanta 200 FEG) operated at an accelerating voltage of 10.0 kV. Transmission electron microscopy (TEM) images of the samples were recorded by a high resolution TEM (JEOL 2010), operated at an acceleration voltage of 200 kV. Raman spectra of the samples were recorded on a LabRAM HR800 confocal microscope Raman system (Horiba Jobin Yvon) using an Ar ion laser operating at 632 nm. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, America) equipped with Al K $\alpha_{1,2}$ monochromatized radiation at 1486.6 eV X-ray source. The surface area and porosity of samples were measured by a Surface Area and Porosity Analyzer (Tristar

3020M).

2.4 Electrochemical measurements

All the electrochemical measurements were performed on an electrochemical workstation (CHI 760D, CH Instruments, Inc., Shanghai, China) and a PINE rotating disk electrode (RDE) system (Pine Instruments Co. Ltd. USA). A conventional three-electrode cell, composed of a catalyst coated glassy carbon (GC) working electrode, an Ag/AgCl reference electrode and a platinum wire counter electrode, was applied to perform electrochemical measurements. The potentials *vs.* Ag/AgCl (4.0 M KCl) were converted to the reversible hydrogen electrode (RHE) using the following relationship [20].

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E^{\circ}_{\text{Ag/AgCl}}$$

where E_{RHE} is the converted potential *vs.* RHE, $E^{\circ}_{\text{Ag/AgCl}} = 0.205$ V at 25°C, and $E_{\text{Ag/AgCl}}$ is the experimentally measured potential against Ag/AgCl reference. A rotating disk electrode (RDE) with a diameter of 5.0 mm was served as the substrate for the working electrode. The electrolyte was 0.1 M KOH solution prepared from deionized water.

Prior to use, RDE (5.0 mm in diameter) was polished with 5.0, 0.3 and 0.05 μm alumina slurry, sequentially, and then washed ultrasonically in ethanol and deionized water for a few minutes, respectively. 4.0 mg catalyst was dispersed ultrasonically in 1000 μL of solvent mixture of Nafion (5%), absolute ethanol, deionized water (V:V:V=1:1:8), to obtain a well-dispersed catalyst ink. Subsequently, 20 μL of catalyst ink was cast onto the glassy carbon (GC) electrode surface and dried at room

temperature for further use. The electrochemical impedance spectroscopy (EIS) measurements were performed by applying an AC voltage with 5 mV amplitude in a frequency range from 100,000 to 10 Hz and recorded at 0.62 V vs. RHE electrode.

ORR measurements: The cyclic voltammogram (CV) tests were performed between 0.17 V and 1.17 V (vs. RHE) at room temperature in N₂- and O₂-saturated 0.1 M KOH solution with a scan rate of 50 mV s⁻¹. RDE experiments were carried out in an O₂-saturated 0.1 M KOH solution at room temperature, a sweep rate of 10 mV s⁻¹ under different rotating rates (400, 625, 900, 1225 and 1600 rpm). All the potentials in this study were reported with respect to the RHE reference electrode. Commercial 20 wt.% platinum on carbon black (Pt/C from Alfa Aesar) was used for comparison, with all the testing parameters kept the same as those used for the N-PC@G electrode.

The electron transfer number (*n*) *per* oxygen molecule at different potentials during the oxygen reduction reaction (ORR) was calculated based on the Koutecky-Levich (K-L) equation [32]:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

$$B = 0.2nFC_0(D_0)^{2/3}\nu^{-1/6}$$

$$J_K = nFkC_0$$

where *J* is the measured current density, *J_L* and *J_K* are the diffusion- and kinetic-limiting current densities, *ω* is the rotation speed, *n* represents the number of electrons transferred *per* oxygen molecule, *F* is the Faraday constant (96485 C mol⁻¹), *C₀* is the O₂ concentration in the electrolyte (1.26×10⁻⁶ mol cm⁻³), *D₀* is the diffusion

coefficient of O₂ in the electrolyte ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), and ν is the kinetic viscosity ($0.01 \text{ cm}^2 \text{ s}^{-1}$)

OER measurements: Oxygen evolution experiments were measured in 0.1 M KOH solution by purging with O₂ for at least 30 min before the measurement. Polarization curves were obtained by sweeping the potential from 1.0 to 1.7 V (vs. RHE) with a sweep rate of 10 mV s^{-1} at 1600 rpm. The OER potential was obtained by iR compensation approach using the $E-iR \times 0.95$ relation, where i is the current and R is the uncompensated electrolyte ohmic resistance, and the resistance of the electrolyte was measured using the catalyst-loaded RDE in 0.1 M KOH solution, and determined to be 48Ω by iR compensation method.

3. Results and discussion

Because of good solubility, wide-open nature and surface rich O-containing functional groups (*e.g.*, -OH and -COOH), graphene oxide (GO) sheets have been recently investigated as both structure-directing and size-controlling substrates for MOFs growth [17, 33, 34]. Moreover, the size and morphology of MOFs are closely related to the GO content in reaction precursors. Fig. 2 shows the powder X-ray diffraction (XRD) patterns of as-prepared samples (ZIF-8 and ZIF-8@GO). As shown, all diffraction peaks of the investigated samples are assigned to pure-phase ZIF-8 crystal data reported [35], indicating successful fabrication of ZIF-8 nanocrystals. Compared to pure ZIF-8 sample (black line), no significant change in diffraction peaks except for peak intensity can be observed for ZIF-8@GO sample (take ZIF-8@GO-0.02 as an example), revealing that the introduction of GO has not

significant influence on ZIF-8 crystalline structure.

Fig. 2 XRD patterns of as-prepared ZIF-8 and ZIF-8@GO-0.02 samples. The red line is the simulated diffraction patterns of pure ZIF-8 nanocrystals.

The morphologies of as-prepared ZIF-8 and ZIF-8@GO (take ZIF-8@GO-0.02 as an example) were characterized *via* field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) techniques, as shown in **Fig. 3**. The results demonstrate that pure ZIF-8 sample is composed of uniform particle-like nanocrystals with sizes in the range of 20~60 nm (**Fig. 3a, b**) [36]. After introduction of GO sheets, ZIF-8@GO-0.02 sample exhibits obvious nanoparticle-covered sheet-like structure, as shown in **Fig. 3c** and inset. Further TEM analysis indicates that ZIF-8@GO-0.02 sheet-like structure is mainly consisted of ZIF-8 nanocrystals and GO sheet (**Fig. 3d**), moreover uniformly dispersed ZIF-8 nanocrystals almost fully cover on both surfaces of GO sheets to form sandwich-like structured composite. Such a sandwich-like structure is very beneficial for preventing graphene sheet agglomeration during high temperature pyrolysis [17]. Further,

high-magnification TEM image of ZIF-8@GO-0.02 (inset in Fig. 3d) reveals that the sizes of ZIF-8 nanocrystals covered on GO sheet are mainly ranging from 20 nm to 60 nm, similar with pure ZIF-8 nanocrystals. Combining with XRD analysis aforementioned, the above results demonstrate that ZIF-8 nanocrystals were successfully grown onto both surfaces of GO sheets to form sandwich-like structured composite. In this work, it was found that GO amount in reaction precursors has important influence on resulting morphology and structure of ZIF-8@GO composite. Although sandwich-like structured composite can still be achieved when increasing GO amount in reaction precursors, the amount of ZIF-8 nanocrystals covered on GO sheet obviously reduces with increasing GO amount (*e.g.*, 0.05 g, 0.1 g), resulting in not fully covered GO surface (Fig. S1a, b and Fig. S2a, b). This may lead to significantly decreased electrocatalytic performance of corresponding pyrolytic carbon product as electrocatalyst. GO surfaces' -OH and -COOH functional groups can coordinate with Zn^{2+} in reaction precursors, providing a reaction platform for the nucleation and growth of ZIF-8 nanocrystals [34]. When the amount of Zn^{2+} and N-containing organic ligands in reaction precursors is fixed, an increase in GO amount would result in a decrease of ZIF-8 nanocrystal amount on both surfaces of each GO sheet, thus a not fully covered GO surface. The above results demonstrate the important role of GO sheets as both structure-directing and size-controlling substrates for controllable growth of ZIF-8@GO composite. Moreover, a suitable GO amount in reaction precursors is critically important for constructing sandwich-like structured composite with fully covered GO surface by ZIF-8 nanocrystals, which

may be favorable for improving electrocatalytic performance of corresponding pyrolytic carbon product when used as electrocatalyst.

Fig. 3 SEM (a) and TEM (b) images of pure ZIF-8 nanocrystals. SEM (c) and TEM (d) images of ZIF-8@GO composite. Insets of corresponding high magnification SEM and TEM images.

Fig. 4 shows the SEM and TEM images of pyrolytic carbon product (N-PC@G) derived from ZIF-8@GO composite at 900 °C under N₂ atmosphere (take N-PC@G-0.02 derived from ZIF-8@GO-0.02 as an example), followed by acid etching. As shown in **Fig. 4a**, the pyrolytic carbon product shows well-preserved sheet-like structure with surface carbon nanoparticles derived from ZIF-8 nanocrystals. TEM image of N-PC@G-0.02 indicates detailed structure information on the pyrolytic carbon product, confirming the composite is composed of graphene sheets and surface carbon nanoparticles (**Fig. 4b**). Compared to ZIF-8 nanocrystals before pyrolysis, the thermally converted carbon nanoparticles show obviously

decreased particle sizes possibly owing to structural shrinkage during high temperature pyrolysis (Fig. 4b). After high temperature pyrolysis, the obtained carbon nanoparticles almost completely cover on both surfaces of graphene sheet with a strong connection to form sandwich-like structured composite. Such structural and component properties are very favorable for improving material's electrical conductivity, thus high electrocatalytic performance when used as electrocatalyst [7, 8]. In previous reports, it has been demonstrated that GO can effectively affect the carbonization process of ZIF, and prevent the agglomeration of carbon structures derived from ZIF and graphene sheets during high temperature pyrolysis process [17]. Our study further confirms this. The high resolution TEM image of an individual carbon nanoparticle derived from ZIF-8 on graphene shows that the carbon nanoparticle consists of nanoporous carbon layers with highly distorted graphitic lattice structure (Fig. 4c and d). The carbon nanoparticles with highly distorted graphitic lattice structure mean more defects, thus possibly providing more catalytic active sites for high performance electrocatalysis applications [11]. Also, corresponding pyrolytic products derived from ZIF-8@GO composites with different GO amounts in reaction precursors were investigated in this work. Similarly, the amount of ZIF-8 derived carbon nanoparticles on the surface of graphene sheet obviously decreases with increasing GO amount in reaction precursors (Fig. S1c, d and Fig. S2c, d). This further verifies that a suitable GO amount in reaction precursors is vital to constructing sandwich-like structured carbon composite with ZIF-8 derived carbon nanoparticles fully covered graphene.

Fig. 4 SEM (a) and TEM (b, c, d) images of as-prepared N-PC@G-0.02 composite. Inset of high magnification SEM image of as-prepared N-PC@G-0.02 composite.

Fig. 5a shows the XRD patterns of the prepared N-PC@G-0.02 sample. For comparison, N-doped porous carbon (N-PC) derived from pure ZIF-8 nanocrystals was also investigated by XRD technique in this work. All investigated samples exhibit graphitic diffraction peaks at around 25.4° , corresponding to the graphitic carbon (002) diffraction [37]. No diffraction peaks of Zn impurities were observed in N-PC@G-0.02 sample, indicating a complete removal of Zn-related species by acid washing approach. Further, N-PC@G-0.02 and N-PC samples were also characterized by the Raman spectrum technique (**Fig. 5b**). The Raman spectrum of N-PC@G-0.02 (black line) displays two conspicuous diffraction peaks at near 1580 cm^{-1} of the G band and 1352 cm^{-1} of the D band, corresponding to the E_{2g} vibration of the sp^2 -bonded carbon atoms and the disordered graphitic carbon, respectively, which are the characteristics of graphitic-like materials [38]. The ratio of the D and G band

intensities (I_D/I_G) is generally used as a measure of carbon disorder, and a high I_D/I_G value indicates high defects in the carbon structure. The I_D/I_G values shown in Fig. 5b are 1.07 and 1.06 for N-PC@G-0.02 and N-PC, respectively, indicating the presence of a great deal of disordered carbon in the obtained carbon structures, which is consistent with high resolution TEM result (Fig. 4d). The presence of a great deal of disordered carbon in N-PC@G-0.02 means more defects, possibly generating more catalytic sites for high efficiency electrocatalysis [11].

Many studies have revealed that the level and type of nitrogen atoms doped in carbon lattice are crucial for promotion of the electrocatalytic performance, and pyridinic nitrogen and graphitic nitrogen are generally considered as the catalytic active sites for ORR [39, 40]. The X-ray photoelectron spectroscopic (XPS) measurements were conducted to investigate the chemical composition and nitrogen bonding configurations of N-PC@G-0.02 obtained at 900 °C. The surface survey XPS spectra of N-PC@G-0.02 reveal the presence of C, N and O elements (Fig. S3). The high-resolution N 1s XPS spectra (Fig. 5c) indicate that the complex N1s spectra can be deconvoluted into four peaks centered at *ca.* 398.4 eV, 399.8 eV, 400.8 eV, and 403.1eV, corresponding to pyridinic-N, pyrrolic-N, graphitic-N, and oxidized N, respectively [11, 28]. A total N doping content of 4.42 at.% can be obtained based on XPS analysis (Table S1), and relative contents of the four types of N doping species were calculated from their corresponding fitted peaks as 35.8, 25.3, 26.5, and 12.4 at.% for pyridinic-N, pyrrolic-N, graphitic-N and oxidized-N, respectively, indicating the successful doping of nitrogen atoms in carbon lattice. Apparently, pyridinic-N and

graphitic-N are predominant among all four doped N types, favorable for high ORR performance [41, 42]. More importantly, N-doped graphene in N-PC@G composite can be concurrently obtained during high temperature pyrolysis owing to the presence of N-containing organic ligands in reaction precursors. To further confirm this, N-doped graphene (N-G) was fabricated by pyrolyzing 100 mg GO and 1.0 g ZIF-8 which were separately placed in two different quartz boats next to each other at 900 °C for 5 h at a heating rate of 5 °C min⁻¹ under N₂ atmosphere. XPS results demonstrate a successful N doping in graphene structure by this approach, as shown in Fig. S4. Such N-doped graphene in N-PC@G composite cannot only effectively improve the electrical conductivity of composite, also provide more catalytic active sites owing to N doping for high efficiency ORR [8]. Fig. 5d shows the N₂ sorption-desorption isotherm and pore size distribution of N-PC@G-0.02 sample. The isotherm of N-PC@G-0.02 exhibits a type-IV curve with a high Brunauer-Emmett-Teller (BET) surface area of 1094.3 m² g⁻¹ and a pore volume of 0.907 cm³ g⁻¹. The high nitrogen uptakes at the low relative pressure and H1 hysteresis loop of isotherm indicate both micropores and mesopores existed in N-PC@G-0.02, which can be further confirmed by pore size distribution analysis (inset in Fig. 5d). As shown, there exist two pore-size distributions in N-PC@G-0.02 sample, concentrated at around 1.8 nm and 10 nm, respectively, confirming the presence of bimodal-pore structure (micropores and mesopores). The micropore size at around 1.8 nm may be due to the microporous structure of carbon nanoparticles inherited from micropore structured ZIF-8 nanocrystals during pyrolysis, while the mesoporous structure of

N-PC@G-0.02 may be originated from the interspaces between carbon nanoparticles. The large surface area ($1094.3 \text{ m}^2 \text{ g}^{-1}$) and bimodal-pore structure (micropores and mesopores) of N-PC@G-0.02 meet the need for high active loading and superior mass transport, thus contributing high electrocatalytic activity [26, 43].

Fig. 5 (a) XRD patterns of the prepared N-PC@G-0.02 and N-PC samples. (b) Raman spectra of the prepared N-PC@G-0.02 and N-PC samples. (c) High resolution N1s XPS spectra of N-PC@G-0.02 sample. (d) N₂ sorption-desorption isotherm of the N-PC@G-0.02 sample; the inset of the corresponding pore-size distribution.

The above results demonstrate that the obtained N-PC@G derived from ZIF-8@GO possesses the required characteristics for a high efficiency carbon-based ORR electrocatalyst [11, 43]. Therefore, the electrocatalytic activities of the

fabricated samples for ORR are evaluated by a three-electrode electrochemical system. To obtain meaningful comparison, N-doped porous carbon (N-PC) derived from pure ZIF-8 nanocrystals, N-PC@G- X ($X=0.02, 0.05, 0.1$ g) obtained from pyrolysis of ZIF-8@GO- X ($X=0.02, 0.05, 0.1$ g), and commercial Pt/C catalysts, are measured under identical conditions. The CV responses (Fig. 6a) of all catalyst coated GC electrodes in O₂-saturated 0.1 M KOH solution exhibit well-defined oxygen reduction peaks at 0.71 V, 0.70 V, 0.71 V, 0.72 V and 0.78 V (vs. RHE) for N-PC, N-PC@G-0.1, N-PC@G-0.05, N-PC@G-0.02 and commercial Pt/C catalysts, respectively, indicating a good ORR electrocatalytic activity of N-PC@G-0.02. Fig. 6b shows the linear sweep voltammetric (LSV) responses of N-PC, N-PC@G- X ($X=0.02, 0.05, 0.1$ g) and commercial Pt/C coated GC electrodes in an O₂ saturated 0.1 M KOH electrolyte under a rotation rate of 1600 rpm. Apparently, N-PC@G-0.02 sample exhibits a half-wave potential of 0.80 V superior to that of commercial Pt/C electrode (0.78 V) and much better than N-PC (0.67 V), N-PC@G-0.1 (0.71V) and N-PC@G-0.05 (0.79V), respectively, indicating a minimal ORR overpotential obtained from N-PC@G-0.02 catalyst. Moreover, the limiting current density (J_L) of N-PC@G-0.02 electrode within a wide potential range is comparable to that of commercial Pt/C catalyst and much better than that of other investigated catalysts, further indicating a superior ORR activity of N-PC@G-0.02. Compared to other catalysts including commercial Pt/C (onset potential of 1.0 V), the onset potential (1.01 V) of N-PC@G-0.02 toward ORR is more positive, indicating a better intrinsically thermodynamic catalytic capability [14, 25]. The above results

demonstrate that the introduction of graphene in ZIF-8 derived carbon composite can significantly improve its ORR performance, moreover, GO amount in reaction precursors has an important influence on resulting ORR catalytic performance of catalyst.

The transferred electron number involved in an ORR process is an important parameter to evaluate the ORR performance of an electrocatalyst, which can be determined by Koutecky-Levich (K-L) equations, as shown in experimental section.

Fig. 6c shows the LSV responses of the N-PC@G-0.02 coated GC electrode obtained from an O₂-saturated 0.1 M KOH solution under different rotation rates. An increase in the cathodic current with the rotation rate indicates a mass transfer controlled process [32]. The linearity of K-L plots for N-PC@G-0.02 derived from Fig. 6c indicates first-order reaction kinetics with regard to the concentration of dissolved oxygen and similar electron transfer numbers at various potentials (Fig. 6d). The average value of transferred electron number ($\bar{n}$) at 0.27 V~0.57 V is calculated to be *ca.* 3.93 (Fig. 6e), close to the theoretical value of Pt/C catalyst ($\bar{n}$ =3.97, Fig. S5), indicating a near 4e ORR pathway. In contrast, the average values of transferred electron number ($\bar{n}$) are calculated to be *ca.* 2.69, 3.37 and 3.61 for N-PC, N-PC@G-0.1 and N-PC@G-0.05 coated GC electrodes under identical experimental conditions, respectively (Fig. S6-S8), further indicating a high ORR electrocatalytic activity of N-PC@G-0.02. The superior ORR catalytic activity of N-PC@G-0.02 was also confirmed from a smaller Tafel slope, as shown in Fig. 6f. At low potentials, the N-PC@G-0.02 shows a Tafel slope of 66 mV dec⁻¹, which is slightly better than that

of commercial Pt/C catalyst (68 mV dec^{-1}) and approaches the theoretical value of 60 mV dec^{-1} obtained by $-2.303RT/aF$ at room temperature (where R is the universal gas constant, a is transfer coefficient, F is the Faraday constant, and T is the absolute temperature). Further, the Tafel slope of N-PC@G-0.02 is also dramatically smaller than that of N-PC (113 mV dec^{-1}), N-PC@G-0.1 (91 mV dec^{-1}) and N-PC@G-0.05 (85 mV dec^{-1}) catalysts, demonstrating a superior kinetic process of N-PC@G-0.02 for ORR. Table 1 shows the detailed electrochemical measurement information on N-PC, N-PC@G- X ($X = 0.02, 0.05, 0.1 \text{ g}$) and commercial Pt/C catalysts for ORR. By comparison, the N-PC@G-0.02 obtained in this work displays much better ORR performance than most of recently reported other and MOFs derived carbon-based electrocatalysts (Table S2).

Table 1 Electrochemical properties of the ORR electrocatalysts in O_2 -saturated 0.1 M KOH electrolyte.

Electrocatalyst	Onset potential [V] (vs. RHE)	Half-wave potential [V] (vs. RHE)	$\bar{n}$ (Average number of electron transfer at $0.27 \text{ V} \sim 0.57 \text{ V}$)
N-PC	0.96	0.67	2.69
N-PC@G-0.1	0.91	0.71	3.37
N-PC@G-0.05	0.95	0.79	3.61
N-PC@G-0.02	1.01	0.80	3.93
Pt/C	1.00	0.78	3.97

Fig. 6 (a) CV curves of ZIF-8 derived carbon and commercial Pt/C catalysts in O_2 saturated 0.1 M KOH solution at a scan rate of 50 mV s^{-1} . (b) LSV curves of ZIF-8 derived carbon and commercial Pt/C catalysts in O_2 -saturated 0.1 M KOH solution at a scan rate of 10 mV s^{-1} and a rotating rate of 1600 rpm. (c) LSV curves of N-PC@G-0.02 catalyst in O_2 -saturated 0.1 M KOH solution at different rotation rates with a sweep rate of 10 mV s^{-1} . (d) Koutecky-Levich plots of N-PC@G-0.02 catalyst at different potentials derived from Fig. 6c. (e) Electron transfer number of N-PC@G-0.02 at 0.27 V~0.57 V. (f) Tafel plots of ZIF-8 derived carbon and commercial Pt/C catalysts.

Fig. 7 (a) Chronoamperometric responses of N-PC@G-0.02 and Pt/C catalysts obtained at 0.62 V in O₂-saturated 0.1 M KOH solution with a rotation rate of 1600 rpm. (b) Chronoamperometric responses of N-PC@G-0.02 and Pt/C catalysts by introducing 3.0 mL of methanol after 400 s.

The durability is also an important parameter for evaluating an ORR electrocatalyst. **Fig. 7a** shows the stability test of N-PC@G-0.02 and Pt/C catalysts in an O₂-saturated 0.1 M KOH solution. N-PC@G-0.02 coated GC electrode exhibits 14% decrease over 20,000 s of continuous operation at a rotation rate of 1600 rpm, while Pt/C coated GC electrode displays a faster current loss with 29% decrease under identical experimental conditions. Further, N-PC@G-0.02 and Pt/C coated GC electrodes were also tested by introducing small fuel molecule (*e.g.*, methanol) into electrolyte to evaluate the possible crossover effect. As shown in **Fig. 7b**, the ORR activity of N-PC@G-0.02 coated GC electrode is almost unaffected, whereas Pt/C coated GC electrode shows a significant current decrease when methanol introduced, suggesting that the N-PC@G-0.02 possesses high ORR selectivity with strong tolerance to methanol crossover effect and high stability. The above results demonstrate that the N-PC@G-0.02 possesses better stability in the alkaline media

and higher resistance to the methanol crossover effect when compared with the commercial Pt/C.

So far, heteroatom doped/co-doped (*e.g.*, N, S, P, B) metal-free carbon materials have been widely investigated as high performance ORR catalysts, whereas only few recent reports demonstrate these metal-free carbon materials as bifunctional electrocatalysts for ORR and OER applications [2, 28-30]. To the best of our knowledge, almost few reports have demonstrated using MOFs derived metal-free carbon materials as bifunctional electrocatalysts for ORR and OER. In this work, the electrocatalytic OER activity of N-PC, N-PC@G-*X* (*X*=0.02, 0.05, 0.1 g), Pt/C and RuO₂ catalysts was also evaluated in a three-electrode system by polarization experiments with the potential extended to the water oxidation regime (1.0 V to 1.7 V, *vs.* RHE). The good catalytic activity of a high performance OER catalyst can be reflected by its comparable onset potential and current density to commercial OER catalysts (*e.g.*, RuO₂, Pt/C). As shown in Fig. 8a, N-PC@G-0.02 coated GC electrode in 0.1 M KOH electrolyte exhibits much higher OER current density than that obtained by N-PC, N-PC@G-0.05 and N-PC@G-0.1 coated GC electrodes, which is comparable to commercial RuO₂ OER catalyst and dramatically better than commercial Pt/C catalyst, indicating a superior OER performance of N-PC@G-0.02. It has been widely accepted that the potential required to oxidize water at the current density of 10 mA cm⁻² is commonly adopted to evaluate the OER activity of an electrocatalyst [28, 44]. As shown in Fig. 8a, the potentials at the current density of 10 mA cm⁻² can be achieved to be 1.63 V and 1.60 V for N-PC@G-0.02 and commercial

RuO₂, respectively, while other electrocatalysts (N-PC, N-PC@G-0.05, N-PC@G-0.1 and Pt/C) display much higher potentials. Apparently, N-PC@G-0.02 catalyst can afford a current density of 10 mA cm⁻² at much lower overpotential than that obtained by other ZIF-8 derived carbon materials, and comparable to the commercial RuO₂ catalyst, further indicating a superior OER activity of N-PC@G-0.02. Fig. 8b shows the Tafel slopes of ZIF-8 derived carbon and commercial RuO₂ and Pt/C catalysts. As shown, the obtained Tafel slope for N-PC@G-0.02 is *ca.* 78 mV dec⁻¹, which is significantly smaller than that of N-PC (176 mV dec⁻¹), N-PC@G-0.05 (212 mV dec⁻¹), N-PC@G-0.1 (365 mV dec⁻¹) and commercial Pt/C (252 mV dec⁻¹) catalysts, and close to commercial RuO₂ catalyst (84 mV dec⁻¹), further confirming the superior OER performance of N-PC@G-0.02.

Fig. 8 (a) OER polarization currents of N-PC, N-PC@G-0.1, N-PC@G-0.05, N-PC@G-0.02, RuO₂ and Pt/C electrodes in 0.1 M KOH solution at a scan rate of 10 mV s⁻¹. (b) Tafel plots of all investigated OER catalysts derived from (a).

The above results have demonstrated the ZIF-8@GO derived metal-free carbon material (*e.g.*, N-PC@G-0.02) possessing superiorly bifunctional catalytic capability toward ORR and OER. Recently experimental and theoretical results have revealed

that N doping and N, P (or N, S) co-doping in carbon structures (*e.g.*, graphene/carbon nanotubes, porous carbon foam) can effectively decrease the overpotentials to facilitate their ORR and OER applications as bifunctional electrocatalysts [2, 28-30]. In this work, the superior ORR and OER performance of N-PC@G-0.02 catalyst may be due to following attributes: (1) ZIF-8 derived N-doped porous carbon structures fully cover on both surfaces of N-doped graphene sheets with an apt amount to form a sandwich-like network structure, which possesses ultrahigh surface area with hierarchical porous structure, facilitating quick mass transfer and high active loading; (2) the formation of N-doped porous carbon and N-doped graphene in N-PC@G-0.02 composite during high temperature pyrolysis may synergistically create more catalytic active sites for ORR and OER; (3) N-doped graphene sheets in N-PC@G-0.02 composite not only provide more catalytic active sites during oxygen reactions, but also act as substrates to efficiently facilitate electrical conductivity, thus improving ORR and OER performance; this superior electrical conductivity of N-PC materials without and with graphene has been indicated by the electrochemical impedance spectrum (EIS) (Fig. S9), and a smaller semicircular diameter of N-PC@G-0.02 compared to N-PC reveals smaller contact and charge transfer impedance of N-PC@G-0.02 due to the introduction of graphene in composite, further verifying the significant role of graphene as conductive substrate. The structural and compositional properties mentioned above of the ZIF-8@GO derived metal-free carbon composite may collectively contribute high ORR and OER performance as a bifunctional electrocatalyst.

4. Conclusion

In summary, we have developed a facile method to fabricate N-PC@G bifunctional electrocatalyst derived from ZIF-8@GO composite obtained by in situ controllable growth of ZIF-8 nanocrystals on both surfaces of graphene oxide sheets. The as-fabricated N-PC@G-0.02 possesses large surface area and hierarchically porous structure, facilitating high active loading and quick mass transfer when used as electrocatalyst. The experimental results demonstrate that such electrocatalyst exhibits excellent bifunctional catalytic activity for both ORR and OER. This work provides an ideal strategy to design and fabricate sandwich-like structured N-doped porous carbon@graphene hybrid materials with large surface area and superior electron transfer property for high performance electrocatalysis applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/>

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