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Melamine-assisted synthesis of atomically dispersed Fe sites anchored on crumple-rich carbon nanospheres as highly efficient electrocatalysts for oxygen reduction reaction

Yuanyuan Cong^{1,2} · Guihui Xie^{1,2} · Xiangzhi Meng^{1,2} · Haibin Wang^{1,2} · Fanchao Meng^{1,2} · Chunlei Li^{1,2} · Qiuping Zhao^{1,2}

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Abstract

Fabrication of an advanced electrocatalyst for oxygen reduction reaction (ORR) is important for the commercialization of fuel cells. Herein, we report an ORR electrocatalyst with Fe atoms evenly distributed on crumple-rich nitrogen-doped carbon (N–C) nanospheres via a simple melamine-assisted pyrolysis strategy, where crumple-rich N–C nanospheres are prepared by a dual soft template approach. The as-obtained Fe–N-C-M electrocatalyst shows a better onset potential (1.02 V vs. RHE) and half-wave potential (0.883 V vs. RHE) in alkaline solution, superior to the commercial Pt/C (0.97 and 0.860 V vs. RHE, respectively). Moreover, the Fe–N-C-M also displays outstanding stability with 80.4% of relative current remained after a 10-h stability test at 0.8 V vs. RHE and remarkable methanol tolerance with 79.2% of relative current sustained after adding 3 M methanol, outperforming the commercial Pt/C (49.4% and 48.5%, respectively). All of these excellent properties are contributed to the unique crumple-rich structure, large specific surface area, and high content of Fe-N_x and pyridinic-N active centers.

Keywords Oxygen reduction reaction \cdot Fuel cells \cdot Crumple-rich \cdot Nitrogen-doped carbon nanospheres \cdot Melamine-assisted pyrolysis

Introduction

Fuel cells are considered as an attractive approach for converting chemical energy into electricity due to their high efficiency and zero tailpipe emissions [1, 2]. The hydrogen fuel cell consists two half-cell reactions: oxygen reduction reaction (ORR) at the cathode side and hydrogen oxidation reaction (HOR) at the anode side [3]. Recently, hydroxide exchange membrane fuel cells (HEMFCs) are gaining wide interest in that they have lower corrosive environments in comparison with proton exchange membrane fuel cells

Yuanyuan Cong and Guihui Xie contributed equally to this work

Qiuping Zhao zqp_lz@163.com (PEMFCs) [4] and with significant progress in alkaline exchange membrane study [5, 6], such as non-Pt electrocatalysts for anodic HOR in alkaline media [7, 8]. Nevertheless, HEMFCs with high performance rely on expensive Ptbased ORR electrocatalysts [9, 10]. Therefore, great efforts have been devoted to explore non-precious metal electrocatalysts whose electrocatalytic activity is comparable or even superior to that of Pt-based electrocatalysts, including heteroatom-doped carbon [11, 12], metal oxides [13], metal carbides [14], metal sulfides [15], metal phosphide [16] materials, and so on.

Among them, the nitrogen-coordinated transition metal supported on a carbon support (M–N-C, M=transition metal), especially Fe–N-C materials, is widely regarded as one of the most promising candidates [17, 18]. Accordingly, the design of Fe–N-C materials depends on both atomically dispersed Fe-N_x sites and excellent carbon architecture. The rational carbon structure is beneficial to the exposure of active sites and the enhancement of mass transfer, improving ORR performance [19].

¹ School of Petrochemical Technology, Lanzhou University of Technology, Lanzhou 730050, Gansu, China

² Key Laboratory of Low Carbon Energy and Chemical Engineering of Gansu Province, Lanzhou University of Technology, Lanzhou 730050, Gansu, China

Compared with the previously reported Fe-N-C electrocatalysts with irregular carbon structure, carbon nanosphere electrocatalysts with porous structure could not only stabilize the Fe-N_x active sites due to large specific surface area, but also prevent the chronic aggregation in practical application based on steady architecture [20]. Recently, Fe-N co-doped porous carbon nanosphere electrocatalyst has been reported to possess a higher activity and stability during ORR [21]. Another work reported about melamine-assisted synthesis of electrocatalysts can incorporate N into the precursor and host a high number of active sites [22]. Therefore, modulating active sites of carbon nanosphere electrocatalysts with melamine may provide a new method for fabricating advanced carbon materials with high performance. However, the preparation of atomic Fe-dispersed N-doped carbon nanosphere electrocatalysts assisted by melamine has been rarely reported.

Herein, we synthesize a nitrogen-doped carbon nanosphere with rich crumples via a dual soft template method and then incorporate Fe salts assisted with melamine to improve the distribution of active sites during pyrolysis. The as-obtained Fe–N-C-M electrocatalyst exhibits outstanding ORR activity with a half-wave potential of 0.883 V vs. RHE and an onset potential of 1.02 V vs. RHE. In addition, the Fe–N-C-M electrocatalyst also displays better stability and methanol tolerance compared with the commercial Pt/C. These results demonstrate that the optimization of support structure combined with the use of melamine to modulate active sites of carbon materials as ORR electrocatalysts has individual potential.

Experimental

Materials

Dopamine hydrochloride (purity $\geq 98.0\%$), 1,3,5-trimethylbenzene (TMB, purity $\geq 98.0\%$), and ammonia (purity $\geq 28.0\%$) were obtained from Aladdin Biochemical Technology Co. Ltd. (Shanghai, China). Pluronic P123 (purity, BR), Pluronic F127 (purity, BR) and ferrous sulfate (FeSO₄, purity $\geq 98.0\%$) were received from Macklin Biochemical Co. Ltd. (Shanghai, China). Potassium hydroxide (KOH) (purity $\geq 85.0\%$), sodium hydroxide (NaOH) (purity $\geq 96.0\%$), and melamine (purity $\geq 99.0\%$) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Commercial Pt/C (20 wt%) was obtained from Johnson Matthey Chemical Co. Ltd. (Landon, UK). Ultrapure water (18.2 M Ω •cm at 25 °C) was used throughout all experiments.

Synthesis of Fe–N-C-M

In a typical synthesis of Fe–N-C-M, 0.6 g of dopamine hydrochloride, 0.1 g of P123, 0.3 g of F127, and 1.6 mL of TMB were dispersed in a mixture of 20 mL of water and 20 mL of ethanol by ultrasonication for 30 min to form an emulsion solution. Subsequently, 1.5 mL of ammonia was quickly added into the mixture mentioned above under stirring at 25 °C. After 2 h of reaction, the products were collected by centrifugation and washed three times with ethanol/water mixture at 10,000 rpm for 10 min. The collected products were dried at 80 °C and then heat-treated in N₂ atmosphere at 800 °C for 2 h with a heating rate of 5 °C min⁻¹. The as-prepared carbon nanosphere support (100 mg) was dispersed in 10 mL of FeSO₄ ethanol/water mixed solution (0.2 mM). After 30 min of ultrasonication, the mixture was transferred to a 50 °C water bath for 2 h, in which Fe salts were uniformly loaded on the support. The ethanol/water mixed solution was finally removed with increasing the temperature of the reaction system to 85 °C. The Fe-loaded precursor (75 mg) was uniformly mixed with melamine (300 mg) by grinding in a mortar. Afterwards, the mixture was annealed at 800 °C for 2 h with a heating rate of 5 °C min⁻¹ in an N₂ atmosphere. The finally obtained sample was denoted as Fe-N-C-M.

Fe–N-C-N was prepared by using the same procedures to that of Fe–N-C-M while leaving out melamine. N–C was synthesized without adding both melamine and $FeSO_4$, keeping all other procedures the same as Fe–N-C-M.

Physical characterizations

The X-ray powder diffraction (XRD) patterns were performed using a PANalytical X'pert Pro Diffractometer with Cu K α radiation (40 kV, 100 mA, $\lambda = 0.15432$ nm) in a 2 θ range from 5 to 80° at a scan rate of 5° min⁻¹. X-ray photoelectron spectra (XPS) measurements were recorded on an ESCALAB250xi spectrometer with Al K α source (h ν = 1486.6 eV) at a constant pass energy of 20 eV. The binding energies were calibrated using the C 1 s at 284.6 eV as the reference. Transmission electron microscopy (TEM) images were carried on a JEM2010 electron microscope at 200 kV. Scanning electron microscopy (SEM) were performed on a SU8020 electron microscope at 1 kV. Atomic resolution high-angle annular dark field (HAADF) scanning TEM (STEM) images were carried out on a FEI Themis Z microscope with a probe aberration corrector. The Raman spectra were collected using a micro-Raman spectrometer system (Labram Evolution) with a Raman excitation wavelength of 532 nm. N₂ adsorption-desorption curves were used to analyze the specific surface area of electrocatalysts based on the Brunauer–Emmett–Teller (BET) method, which were measured at 77 K on a Micromeritics TriStar II 3020 instrument. Inductively coupled plasma–optical emission spectroscopy (ICP-OES) (7300DV, PerkinElmer) was used to determine the Fe content.

Electrochemical measurements

All the electrochemical measurements were collected on CHI 760D electrochemical workstation (Shanghai, China) in a three-electrode electrochemical cell with Hg/HgO (1 M NaOH) as the reference electrode, a graphite rod as the counter electrode, and a glassy carbon rotating disk electrode (RDE) with an electrocatalyst layer as the working electrode in 0.1 M KOH ag. The electrocatalyst ink was prepared by dispersing 5.0 mg electrocatalyst in 15.0 µL Nafion solution (5 wt%), 2.25 mL ethanol, and 0.25 mL H₂O under sonication for 10 min. A 120-µL ink was casted onto the RDE, and the electrocatalyst loading was $1.2 \text{ mg}_{cat} \text{ cm}_{disk}^{-2}$ on the working electrode. For comparison, commercial Pt/C (20 wt%) ink was prepared using the similar manner with 10-µL ink casted onto the RDE, and the Pt loading was 10 μg_{Pt} cm^{-2} . All reported potentials in this study were converted to the reversible hydrogen electrode (RHE) via the conversion equation E(RHE) = E(Hg/HgO) + 0.895 V, which was determined by the equilibrium potential of a Pt disk electrode as the working electrode in H₂ saturated 0.1 M KOH aq.

Cyclic voltammetry (CV) test was carried out in both N_2 and O_2 saturated 0.1 M KOH aq. at a scan rate of 50 mV s⁻¹ from 0 to 1.2 V vs. RHE. The ORR activity was evaluated by linear sweep voltammetry (LSV) in O_2 -saturated 0.1 M KOH aq. at a scan rate of 10 mV s⁻¹ from 0 to 1.2 V vs. RHE with a rotation speed of 1600 rpm, if not specific. All LSV electrochemical data were corrected by deducting the background current that measured in N_2 -saturated electrolyte. The relevant transferred electron number (*n*) was calculated by Koutecky–Levich equation as follows:

$$j^{-1} = jK^{-1} + jL^{-1} = jK^{-1} + (B\omega^{0.5})^{-1}$$

$$B = 0.2nFC_0 D_0^{2/3} - v^{1/6}$$

where *j* is the measured current density, j_K is the kinetic current density, j_L is the diffusion-limiting current density, *B* could be determined from the slope of the K-L plots, ω represents rotating rate of electrode expressed in rpm, *F* is the Faraday constant (96,485 C mol⁻¹), C_0 is the bulk concentration of O₂ (1.2×10⁻⁶ mol cm⁻³), D_0 is the diffusion coefficient of O₂ in 0.1 M KOH aq. (1.9×10⁻⁵ cm² s⁻¹), and v is the kinetic viscosity of the electrolyte (0.01 cm² s⁻¹).

The peroxide species yield $(\text{HO}_2^-\% \text{ in alkaline solution})$ and *n* were detected by rotating ring disk electrode (RDDE) testing and then calculated based on the following equations:

$$HO_2^{-\%} = \frac{200I_R/N}{I_D + I_R/N}$$
$$n = \frac{4I_D}{I_D + I_R/N}$$

where I_D and I_R are the Faradaic current at the disk and ring, respectively. N is the collection coefficient (25.6% in this work) at the ring.

The stability of the electrocatalysts was conducted in O_2 -saturated 0.1 M KOH aq. by the current-time (i-t) chronoamperometry technique at 0.8 V vs. RHE with a rotation speed of 1600 rpm for 10 h. The methanol tolerance measurements were assessed by chronoamperometry response before and after the addition of 3 M CH₃OH into O_2 -saturated 0.1 M KOH aq. at 0.8 V vs. RHE.

Results and discussion

The melamine-assisted synthesis of the Fe-N co-doped carbon nanosphere electrocatalyst with rich crumples, denoted as Fe-N-C-M, was illustrated in Fig. 1. The synthetic strategy includes three steps: firstly, polymer complexes were formed by the polymerization assembly of dopamine by ammonia catalysis with Pluronic F127 and Pluronic P123 as the dual soft template for the regulation of pore structure or surface texture and 1,3,5-trimethylbenzene (TMB) as the nanoemulsion in a mixture solution of water/ethanol. The uniform polymer complexes with rich crumples and an average size of 209.9 ± 7.1 nm were obtained by centrifugation and washing (Fig. S1). Secondly, the polymer complexes were heat-treated in N₂ atmosphere at 800 °C for 2 h to obtain carbon nanosphere support, which remains the initial structure and spherical morphology with an average diameter of 205.0 ± 4.9 nm (Fig. S2). The crumple-rich carbon nanosphere support with N species displays negative charge, which can absorb Fe cation of FeSO₄ and avoid the shedding or agglomeration of Fe species [23]. As expected, there is no structural difference before and after Fe salts coated on the carbon support (Figs. S2 and S3). The obtained powder coated with Fe salts was further grinded with melamine, which serves as N source to develop high N-doped electrocatalysts. Finally, the mixture was annealed at 800 °C for 2 h in an N₂ atmosphere, and Fe–N-C-M electrocatalyst was collected. For comparison, Fe-N-C-N was also prepared following the same procedure to that of Fe-N-C-M while leaving out melamine (Fig. S4). N-C was synthesized without the addition of both melamine and Fe salts (Fig. S5, see more details in the Experimental section).

SEM and TEM were used to investigate the morphology and microstructure of the Fe–N-C-M, which possesses spherical morphology with an average size of 203.1 ± 6.6 nm (Fig. 2a–c). Closer observation of the SEM image reveals that each nanosphere exhibits many crumples on it, which Fig. 1 A schematic diagram about the synthesis of atomically dispersed Fe sites anchored on crumple-rich carbon nanospheres: I the coordination to form polymer complexes with rich crumples. II The pyrolysis in N_2 atmosphere, followed by the loading of Fe salts and the coating melamine on carbon nanospheres. III The pyrolysis in N_2 atmosphere to obtain Fe–N-C-M electrocatalyst





Fig.2 a SEM image. b TEM image. c The corresponding histogram of particle size distributions. d HR-TEM image. e-h the HAADF-STEM image and the corresponding elemental mapping images of

the Fe–N-C-M electrocatalyst. **i–k** Aberration-corrected HAADF-STEM images of the Fe–N-C-M electrocatalyst at different magnifications

can effectively anchor and disperse active sites [24]. No Fe-based nanoparticles or clusters are found from the highresolution transmission electron microscopy (HR-TEM); however, the graphite stripes are discernible for the Fe-N-C-M (Fig. 2d). Moreover, the elemental mappings of the Fe-N-C-M display a uniform distribution of Fe and N over the carbon nanosphere, indicating that Fe species may be atomically distributed in the carbon framework (Fig. 2e-h). In contrast, the Fe–N-C-N synthesized without the assistance of melamine shows Fe-based nanoparticles (Fig. S4d). This strongly demonstrates that the incorporation of melamine as a N source plays a crucial role for the realization of control over the active site distribution. In addition, atomically dispersed Fe sites in the Fe-N-C-M electrocatalyst are confirmed by aberration-corrected HAADF-STEM images (Fig. 2i-k). The circled bright dots display the Fe atomically distributed in the carbon matrix. ICP-OES reveals the Fe content is 0.2 wt%.

The XRD pattern of the Fe–N-C-M (Fig. 3a) similar to that of the N-C shows only two broad peaks at 24° and 44°, attributing to the (002) and (101) facet of graphitic carbon, respectively [25]. The absence of Fe-containing nanoparticles peaks for the Fe-N-C-M. However, XRD pattern of the Fe-N-C-N appears Fe₃O₄ (JCPDS, PDF, File no. 26-1136, 65-3107), Fe₃C (JCPDS, PDF, File no. 65-2411), Fe (JCPDS, PDF, File no. 65-4899), and Fe₂O₃ (JCPDS, PDF, File no. 33–0664), which is consistent with the result of TEM images. In the Raman spectra (Fig. 3b), all of the samples (Fe-N-C-M, Fe-N-C-N, and N–C) show two peaks assigned to the D (1340 cm^{-1}) and G (1590 cm^{-1}) peaks, representing the stretch vibration of the disordered sp³-bonded carbon atoms and the graphitic sp²-bonded carbon atoms, respectively [26]. Compared with other electrocatalysts, the Fe–N-C-M exhibits the lowest $I_D/$ I_G value, indicating its higher conductivity arising from the enhancement of graphitization level induced by the incorporation of melamine [27]. The specific electrical resistivity of the Fe–N-C-M detected by four-probe method is 1.1 Ω cm, similar to that of the commercial Pt/C $(1.2 \Omega \text{ cm})$ [28]. N2 adsorption-desorption measurement was used to investigate the textural properties of electrocatalysts [29]. Both the

Fe–N-C-M and the commercial carbon material (VXC-72) exhibit a type IV adsorption isotherm curve, suggesting the presence of mesopores structure [30]. The pore size distribution of the Fe–N-C-M calculated from the desorption branch by the Barrett-Joyner-Halenda model displays a narrower pore size centering at around 3.5 nm compared with the commercial carbon material (Fig. S6). Moreover, the BET surface area of the Fe–N-C-M is 172.0 m² g⁻¹, comparable to the commercial carbon material of 220.5 m² g⁻¹ (Fig. 3c). The mesopore structure and large specific surface area will benefit the improvement of mass transfer, facilitating ORR process [31].

The surface elemental compositions and chemical status of the Fe-N-C-M electrocatalyst were further analyzed by XPS. XPS shows that the deconvoluted C 1 s peaks of Fe-N-C-M at 284.6 and 285.7 eV are assignable to C-C and C-N, respectively (Fig. 4a) [32]. The N 1 s spectrum are deconvoluted into five characteristic components: pyridinic-N (398.2 eV), Fe-N_x (399.6 eV), pyrrolic-N (400.8 eV), graphitic-N (402.1 eV), and oxidized-N (404.1 eV) (Fig. 4b) [33]. It has been well accepted that the pyridinic-N and Fe-N_x are effective active sites in the ORR process [17]. As contrasted in Figs. S7 and S8, the total N content increases to 4.39 at% for the Fe-N-C-M under the addition of melamine compared with the N-C of 2.82 at% and the Fe-N-C-N of 2.47 at%. Furthermore, both the contents of the pyridinic-N (0.68 at%) and Fe-N_x (1.70 at%) in the Fe–N-C-M are much higher than those of other electrocatalysts, indicating melamine-assisted synthesis strategy can host a high number of active sites and favor the formation of the more ORR active sites exposed on the outside (Fig. S8d). The Fe 2p spectrum is fitted into two main peaks at 710.8 and 713.7 eV, assigned to Fe(II) 2p_{3/2} and Fe(III) 2p_{3/2}, respectively (Fig. 4c). Fe only exists as Fe(II) and Fe(III) in the Fe-N-C-M, which is possible in the form of Fe- N_x [19]. The high-resolution Fe 2p spectrum of Fe-N-C-N appears on different peaks at 708.0 eV, corresponding to metal Fe or Fe₃C species (Fig. S8c) [34, 35]. These results further demonstrate the coexistence of the Fe-containing nanoparticles and Fe-N_x active sites for the Fe-N-C-N, whereas the Fe-N-C-M possesses an excellent distribution of Fe-N_x active sites.

Fig. 3 a XRD patterns and b Raman spectra of the N–C, Fe–N-C-N, and Fe–N-C-M electrocatalysts. c N_2 adsorption–desorption isotherms of the VXC-72 and Fe–N-C-M electrocatalysts





Fig. 4 a C 1 s spectrum, b N 1 s spectrum, and c Fe 2p spectrum of the Fe–N-C-M electrocatalyst

The ORR performance was investigated by a glassy carbon rotating disk electrode setup in 0.1 M KOH solution. Figure 5a shows the CV curves of the Fe–N-C-M electrocatalyst recorded in 0.1 M KOH aq. saturated with N_2 and

 O_2 , respectively. Obviously, a rectangle-like curve without the redox peak is detected in N₂-saturated solution. However, a discernible cathodic oxygen reduction peak at $0.8 \sim 1.0$ V vs. RHE is found in O₂-saturated electrolyte, predicting that



Fig. 5 a CV curves of the Fe–N-C-M in 0.1 M KOH aq. saturated with N_2 (dash line) and O_2 (solid line), respectively. b LSV curves of the N–C, Fe–N-C-N, Fe–N-C-M, and commercial Pt/C electrocatalysts in O_2 -saturated 0.1 M KOH aq. at a rotation speed of 1600 rpm. c The half-wave potential and onset potential of the corresponding

electrocatalysts. **d** Koutecky–Levich plots of the Fe–N-C-M. **e** i–t curves of the Fe–N-C-M and commercial Pt/C at 0.80 V vs. RHE. **f** The chronoamperometric response of the Fe–N-C-M and commercial Pt/C before and after the addition of 3 M methanol with a rotation speed of 1600 rpm at 0.80 V vs. RHE

the Fe-N-C-M owns an effective ORR activity [36, 37]. To prove the excellent performance, we investigate the ORR activity by the LSV curves. As shown in Fig. 5b and c, the Fe-N-C-M electrocatalyst displays the most positive onset potential ($E_0 = 1.02$ V vs. RHE) and the highest half-wave potential ($E_{1/2} = 0.883$ V vs. RHE) among all of the electrocatalysts, superior to the commercial Pt/C ($E_0 = 0.97$ V vs. RHE and $E_{1/2} = 0.860$ V vs. RHE), N–C ($E_0 = 0.95$ V vs. RHE and $E_{1/2} = 0.781$ V vs. RHE), and Fe–N-C-N $(E_0 = 1.01 \text{ V vs. RHE} \text{ and } E_{1/2} = 0.870 \text{ V vs. RHE}).$ The Fe–N-C-M electrocatalyst has the high content of the Fe-N_v and pyridinic-N, unique crumple-rich structure, large specific surface area, and good conductivity which should partially explain the best activity. Compared with other Fe-N-C alkaline ORR electrocatalysts in the literature, the Fe-N-C-M represents one of the best performance (Table S1). In order to reveal the ORR pathway of the Fe-N-C-M, the LSV curves with different rotation speeds were tested in O₂-saturated 0.1 M KOH to calculate the transferred electron number (n, Fig. S9a) [38]. The n extracted according to the slope of the Koutecky-Levich curve is 4.0 at 0.3-0.7 V vs. RHE, suggesting that the ORR on Fe-N-C-M similar to the commercial Pt/C is dominated by a direct 4e⁻ process (Fig. 5d and Fig. S9b-d) [39]. RRDE measurements were also performed to study the kinetics of the Fe-N-C-M. The yield of peroxide species is less than 2%, and the *n* is close to 4.0 at 0.1–0.8 V vs. RHE (Fig. S10), further implying that the Fe-N-C-M electrocatalyst precedes a dominant 4e⁻ pathway.

The stability of the electrocatalysts is another key parameter for their potential applications, which was measured via a chronoamperometric response (i-t) and exhibited in Fig. 5e. It can be observed that the relative current of the Fe-N-C reserves 80.4% of its initial value after 10 h at the constant potential of 0.8 V vs. RHE, while the commercial Pt/C only reserves 49.4% under the same condition, indicating the stability of the Fe-N-C-M is better than the commercial Pt/C [40]. To elucidate the superior stability of the Fe-N-C-M, the morphological differences of the electrocatalysts before and after the stability tests were investigated by TEM (Fig. S11). The aged Fe–N-C-M remains the initial nanosphere structure with an original average size of around 200 nm, and no Fe-based nanoparticles are observed. However, Pt nanoparticles of the aged commercial Pt/C seriously aggregate. The excellent stability of the Fe-N-C-M is likely contributed to its unique crumple-rich architecture. In addition to its activity and stability, the methanol tolerance of the Fe-N-C-M was also tested by the i-t curves. After the addition of 3 M methanol at 400 s, the relative current of the Fe–N-C-M at 0.8 V vs. RHE slightly decreases to 79.2% of its initial value. The activity loss may be attributed to the unique crumple-rich structure, which can absorb some methanol and then hinder the adsorption of O_2 [41, 42]. However,

the commercial Pt/C sharply decreases to 48.5%. This confirms that the Fe–N-C-M is more resistant to methanol crossover than that of the commercial Pt/C [43, 44]. Overall, the crumple-rich Fe–N-C-M nanosphere electrocatalyst with remarkable activity, stability, and methanol tolerance is an efficient non-precious metal ORR electrocatalyst.

Conclusions

In summary, we successfully synthesized an atomically dispersed Fe sites anchored on crumple-rich carbon nanosphere electrocatalyst, Fe–N-C-M, by a dual soft template approach with melamine-assisted pyrolysis. Benefiting from the unique crumple-rich structure, large specific surface area, high content of the Fe-N_x, and pyridinic-N active sites, the Fe–N-C-M exhibits remarkable electrocatalytic activity, structural stability, and methanol tolerance. This study presented herein provides a candidate of the highly efficient ORR electrocatalysts and would likely provide a new route to rationally design other efficient transition metal–heter-oatom-doped carbon materials for energy conversion.

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Declarations

Conflict of interest The authors declare no competing interests.

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