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Supporting Information

Nitrogen-doped Fe/Fe₃C@graphitic layer/carbon nanotube hybrids derived from MOFs: efficient bifunctional electrocatalysts for ORR and OER

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Experimental Sections

Materials and Preparation of the catalysts

All reagents were analytical grade and used without further purification. All solutions used in electrochemical experiments were prepared with Millipore water ($\geq 18 \text{ M}\Omega$).

Synthesis of MIL-101 (Fe)

MIL-101 (Fe) was prepared following the protocol described earlier.^[1] In a typical synthesis, 15 mL of N,N-Dimethylformamide (DMF) consisting of FeCl₃·6H₂O, and terephthalic acid (H₂bdc) were thoroughly dissloved with ultrasonication. Subsequently, the solution was heated at 110°C for 20 h in a Teflon reactor. The resulting brown solids were isolated by centrifuging, and were washed with ethanol.

Synthesis of Fe/Fe₃C@C

2 g of MIL-101(Fe) was pyrolyzed in a flow of ultrapure N_2 at 700 °C for 5 h with the heating rate of 10 °C min⁻¹ and denoted as Fe/Fe₃C@C.

Synthesis of Fe/Fe₃C@NC

In a typical procedure, 2 g of MIL-101(Fe) was soaked in a certain amount DMF solution in the presence of melamine for about 12 h. The resulted samples were filtered and pyrolyzed in a flow of ultrapure N_2 at 700 °C for 5 h with the heating rate of 10 °C min⁻¹.

Synthesis of Fe/Fe₃C@NGL-NCNT

2g of MIL-101(Fe) and 2g of melamine were mixed by ball milling. And then, the mixture was pyrolyzed in a flow of ultrapure N₂ at different temperatures (500, 700, 900, and 1100 °C) for 5 h with the heating rate of 10 °C min⁻¹. The obtained samples were defined as C-MIL-101(Fe)-500, Fe/Fe₃C@NGL-NCNT, Fe/Fe₃C@NGL-NCNT-900, and Fe/Fe₃C@NGL-NCNT-1100, respectively.

For comparison, Fe/Fe₃C@NGL-NCNT were acid etched in H_2SO_4 (1 M) by 24 h of continuous agitation at 80 °C to remove unstable and inactive species. The etched samples were then thoroughly washed with de-ionized water until reaching a neutral pH (Fe/Fe₃C@NGL-NCNT after etching).

Characterizations

The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were

recorded on JEOL-2100F apparatus at an accelerating voltage of 200 kV. Surface morphologies of the carbon materials were examined by a scanning electron microscope (SEM, JSM-7600F) at an acceleration voltage of 10 kV. The thermogravimetric analysis (TGA) was performed on PERKINELMER TG synchronous thermoanalysis instruments. The energy-dispersive X-ray spectroscopy (EDS) was taken on JSM-5160LV-Vantage typed energy spectrometer. The powder X-Ray diffraction (XRD) patterns were recorded on a D/max 2500VL/PC diffractometer (Japan) equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.54060$ Å). Corresponding work voltage and current is 40 kV and 100 mA, respectively. X-ray photon spectroscopy (XPS) was recorded by a scanning X-ray microprobe (PHI 5000 Verasa, ULAC-PHI, Inc.) using Al k α radiation and the C1s peak at 284.8 eV as internal standard. The Raman spectra of dried samples were obtained on Lab-RAM HR800 with excitation by an argon ion laser (514.5 nm). The nitrogen adsorption-desorption experiments were operated at 77 K on a Micromeritics ASAP 2050 system. The pore size distributions were measured by the density functional theory (DFT). Prior to the measurement, the samples were degassed at 150 °C for 10 h.

Electrode preparation

All electrochemical experiments were conducted on a CHI 760D electrochemical station (Shanghai Chenhua Co., China) in a standard three electrode cell at room temperature. An Ag/AgCl with saturated KCl, and a Pt wire were used as reference and counter electrode, respectively.

The procedures of glass carbon electrodes (5.0 mm in diameter from Gamry Instruments, USA) preparation were as follows: prior to use, the electrodes were polished mechanically with aluminite power under an chamois, successively washed with ethanol and de-ionized water by sonication for 5 minutes, and dried in a desiccator. 4 mg of the catalysts were dispersed in 2 mL of solvent of Nafion (5%) and de-ionized water (1:9) by sonication, respectively. Typically, 10 μ L (2 mg/mL) well-dispersed catalysts suspensions were pipetted onto the glassy carbon electrode surface and allowed to dry at room temperature for 30 minutes. For comparison, a commercially available Pt-C (20 wt%, Johnson Matthey) catalyst was prepared in the same way.

Cyclic voltammetry experiments (CVs) were performed at room temperature in 0.1 M KOH solutions which were purged with N_2 or O_2 for at least 30 minutes before measuring oxygen reduction reaction (ORR) activity from -1.0 to 0.2 V at a scan rate of 100 mV s⁻¹.

In the rotating disk electrode (RDE) tests, the linear sweep voltammograms (LSVs) were measured in O_2 saturated 0.1 M KOH solution and the potential was varied from 0.2 to -1.0 V with a scan rate of 10 mV s⁻¹ at various rotating speeds from 400 to 1600 rpm.

To examine the ORR performance, the number of electron (n) was conducted according to Koutecky-Levich (K-L) equation:

(1) $j^{-1} = j_L^{-1} + j_k^{-1} = (B\omega^{1/2})^{-1} + j_k^{-1}$

- (2) B = 0.62 n F C_{O2} (D_{O2})^{2/3} v^{-1/6}
- (3) $j_k = n F k C_{O2}$

Where j is the measured current density, j_k and j_L are the kinetic and diffusion-limiting current density, respectively. B is Levich slope which is given by (2). n is the number of electrons transferred for ORR. ω is the rotation rate ($\omega = 2 \pi N$, N is the linear rotation speed), F is the Faraday constant (F = 96485 C mol⁻¹), v is the kinetic viscosity, and C₀₂ is the concentration of O₂ (1.2*10⁻³ mol L⁻¹), and D₀₂ is the diffusion coefficient of O₂ in 0.1 M KOH (1.9*10⁻⁵ cm s⁻¹).

Reference:

N. V. Maksimchuk, K. A. Kovalenko, V. P. Fedin and O. A. Kholdeeva, *Chem. Commun.*, 2012, 48, 6812.

Figures in Supporting Information



Figure S1. (A) Simulated and synthesized PXRD profiles, (B) TGA in a flow of ultrapure N₂, (C) SEM and (D) TEM of MIL-101 (Fe), respectively.

The powder X-Ray diffraction (XRD) pattern of MIL-101 (Fe) is consistent with the simulated (Figure S1A), indicating high crystallinity and phase purity. Thermogravimetric analysis (TGA) of MIL-101 (Fe) was performed under N₂ flowing at a heating rate of 10 °C min⁻¹, which reveals the complete decomposition of MIL-101 (Fe) above 700 °C (Figure S1B).The transmission electron microscopy (TEM) (Figure S1C) and scanning electron microscopy (SEM) (Figure S1D) images show the octahedral crystals of MIL-101 (Fe).



Figure S2. XRD patterns of Fe/Fe₃C@C, Fe/Fe₃C@NC, and Fe/Fe₃C@NGL-NCNT, respectively.



Figure S3. STEM images of Fe/Fe₃C@NGL-NCNT and the corresponding C-, O-, N-, and Fe elemental mappings.



Figure S4. (A, B) SEM and (C, D) TEM images of Fe/Fe₃C@C and Fe/Fe₃C@NC, respectively.



Figure S5. (A) XPS survey spectrum and (B) high-resolution Fe 2p XPS spectrum of Fe/Fe₃C@C, respectively. (C) XPS survey spectrum of Fe/Fe₃C@NGL-NCNT. (D) XPS survey spectrum, (E-F) high-resolution N 1s and Fe 2p XPS spectra of Fe/Fe₃C@NC, respectively.



Figure S6. (A-C) EDS of Fe/Fe₃C@C, Fe/Fe₃C@NC, and Fe/Fe₃C@NGL-NCNT, respectively.



Figure S7. CVs of Fe/Fe₃C@NGL-NCNT in N_2 - or O_2 -saturated 0.1 M KOH solution.



Figure S8. (A) SEM and (B) TEM images of Fe/Fe₃C@NGL-NCNT after etching with graphitic layer (yellow arrows), carbon nano-tube (green arrows), and Fe/Fe₃C (red arrows), respectively.



Figure S9. XRD patterns of Fe/Fe₃C@NGL-NCNT before and after etching.



Figure S10. (A) N₂ sorption isotherms and (B) pore size distributions from DFT method of Fe/Fe₃C@NGL-NCNT before and after etching.



Figure S11. LSV curves of Fe/Fe₃C@NGL-NCNT before and after etching at 1600 rpm in O₂-saturated 0.1 M KOH solution.

From Figure S8, the morphologies of Fe/Fe₃C@NGL-NCNT before and after etching are still remained. Surprisingly, the intensity of peak at 26.2° increases after etching, whereas the other peaks decrease (Figure S9). Additionally, the BET of Fe/Fe₃C@NGL-NCNT after etching (303 cm² g⁻¹) is higher than that of Fe/Fe₃C@NGL-NCNT before etching (210 m² g⁻¹) (Figure S10), due to the removal of partial Fe/Fe₃C species. However, it is worth noting that a negative shift of the onset potential, and slight decrease of current density of Fe/Fe₃C@NGL-NCNT after etching are shown in Figure S11.



Figure S12. (A, C) LSV and (B, D) K-L plots of Fe/Fe₃C@C, and Fe/Fe₃C@NC from -0.4 to -0.8 V, respectively.



Figure S13. CVs at the Pt-C electrode in an O₂-saturated 0.1 M KOH solution or an O₂-saturated 0.1 M KOH solution upon addition of methanol, respectively.



Figure S14. (A-B) Current-time (i-t) chronoamperometric response of $Fe/Fe_3C@NGL-NCNT$ and Pt-C electrodes at -0.4 V and 0.7 V (vs Ag/AgCl) in O₂-saturated 0.1 M KOH at a rotation rate of 1600 rpm for the ORR and OER, respectively.



Figure S15. XRD patterns of the mixture of MIL-101 (Fe) and melamine pyrolyzed at different temperatures, respectively.



Figure S16. (A-D) SEM and (E-H) TEM images of the mixture of MIL-101 (Fe) and melamine pyrolyzed at different temperatures with graphitic layer (yellow arrows), carbon nanotube (green arrows), and Fe/Fe₃C (red arrows), respectively.



Figure S17. Raman spectra of the mixture of MIL-101 (Fe) and melamine pyrolyzed at different temperatures, respectively.



Figure S18. (A) XPS survey spectra and (B-C) high resolution XPS of N and Fe of the mixture of MIL-101 (Fe) and melamine pyrolyzed at different temperatures, respectively.

The mixture of MIL-101 (Fe) and melamine was pyrolyzed at 500, 700, 900, and 1100 °C (defined as C-MIL-101(Fe)-500, Fe/Fe₃C@NGL-NCNT, Fe/Fe₃C@NGL-NCNT-900, and Fe/Fe₃C@NGL-NCNT-1100), respectively. From Figure S15, the XRD of C-MIL-101(Fe)-500 has low graphitic degree, characteristic of amorphous carbon.

Nevertheless, with the increase of pyrolysis temperature, the graphitic degrees of Fe/Fe₃C@NGL-NCNT-900, and 1100 have been improved. These results are further verified by SEM, TEM images (Figure S16), and Raman spectra (Figure S17). As shown in Figure S19, the Fe/Fe₃C@NGL-NCNT exhibits the best electrocatalytic activity for the ORR regardless of the onset potential and current density. However, the inferior performance on the C-MIL-101(Fe)-500 may result from the lower conductivity owing to the uncompleted decomposition of MIL-101 (Fe). In term of Fe/Fe₃C@NGL-NCNT-900, and 1100, as the pyrolysis temperature increases, the lower electrocatalytic activity may be associated to the sintering and aggregation of Fe/Fe₃C species. Simultaneously, the contents of N and Fe significantly decrease, implying the loss of active sites, which are reconfirmed by XPS (Figure S18 and Table S2).



Figure S19. LSVs of the mixture of MIL-101 (Fe) and melamine pyrolyzed at different temperatures at 1600 rpm.

Tables in Supporting Information

| Materials | Elemental composition (at %) | | | | |
|-------------------------------|------------------------------|-----------------|-----------|-----------------|--|
| | C _{1s} | N _{1s} | Fe_{2p} | O _{1s} | |
| Fe/Fe ₃ C@C | 90.52 | 0 | 1.86 | 7.62 | |
| Fe/Fe₃C@NC | 91.97 | 0.58 | 1.61 | 5.85 | |
| Fe/Fe ₃ C@NGL-NCNT | 86.55 | 3.64 | 2.08 | 7.73 | |

Table S1. Elemental compositions of Fe/Fe₃C@C, Fe/Fe₃C@NC, and Fe/Fe₃C@NGL-NCNT determined by XPS, respectively.

Table S2. Elemental compositions of C-MIL-101(Fe)-500, Fe/Fe₃C@NGL-NCNT, Fe/Fe₃C@NGL-NCNT-900 and Fe/Fe₃C@NGL-NCNT-1100 determined by XPS, respectively.

| Materials | Elemental composition (at %) | | | | |
|------------------------------------|------------------------------|----------|-----------|-----------------|--|
| | C _{1s} | N_{1s} | Fe_{2p} | O _{1s} | |
| C-MIL-101(Fe)-500 | 42.17 | 36.26 | 6.52 | 15.06 | |
| Fe/Fe ₃ C@NGL-NCNT | 86.55 | 3.64 | 2.08 | 7.73 | |
| Fe/Fe ₃ C@NGL-NCNT-900 | 89.74 | 1.7 | 1.49 | 7.06 | |
| Fe/Fe ₃ C@NGL-NCNT-1100 | 94.29 | 0.92 | 1.2 | 3.59 | |