Supporting Information

N-Doped graphene analogue synthesized by pyrolysis of metal tetrapyridinoporphyrazine with high and stable catalytic activity for oxygen reduction

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1. Synthesis of the precursor MTAP

1.1 Synthesis of FeTAP

FeTAP was prepared as follow: [1] A mixture of 1.50 g pyridine-2,3-dicarboxylic acid, 6.00 g urea, 1.76g $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ and 0.06 g $(NH_4)_2Mo_2O_7$ in a 100 ml crucible was irradiated in a microwave oven at 460W for 8 min , and then at 800 W for 8 min. After cooling to room temperature, the as-product was washed with water, acetone, and methyl alcohol several times.

After being vacuum dried, the purification of blue solid was done by refluxing with 150 ml of acetone, methyl alcohol, and trichloromethane for about 12 hours, respectively. Then the as-product was recrystallized from concentrated sulfuric acid/water. FeTAP: 47% yield; m.p. >300 ^oC; IR (KBr pellet, cm^{-1}): 1664 (s), 1584 (s), 1515 (m), 1105 (s), 924 (m), 794 (s), 753 (s); UV/Vis (DMSO):λmax=337, 627 nm. Anal. Cald for $C_{28}H_{12}N_{12}Fe$: C, 58.76; H, 2.11; N, 29.37; Found: C, 58.72; H, 2.23; N, 29.42.

1.2 Synthesis of NiTAP

A mixture of 1.50 g pyridine-2,3-dicarboxylic acid, 6.00 g urea, 1.10g $NiCl_2 \cdot 6H_2O$ and 0.06 g $(NH_4)_2Mo_2O_7$ in a 100 ml crucible was irradiated in a microwave oven at 460W for 8 min , and then at 800 W for 8 min. After cooling to room temperature, the as-product was washed with water, acetone, and methyl alcohol several times.

After being vacuum dried, the purification of blue solid was done by refluxing with 150 ml of acetone, methyl alcohol, and trichloromethane for about 12 hours, respectively. Then the as-product was recrystallized from concentrated sulfuric acid/water. NiTAP: 43% yield; m.p.>300 ^oC; IR(KBr pellet, cm^{-1}): 1641 (s), 1579 (s), 1531 (m), 1087 (s), 931 (m), 788 (s), 744 (s); UV/Vis (DMSO):λmax=272, 578 nm. Anal. Cald for $C_{28}H_{12}N_{12}Ni$: C, 58.47; H, 2.10; N, 29.22; Found: C, 58.31; H, 2.43; N, 29.45.

2. The boats in the quartz tube

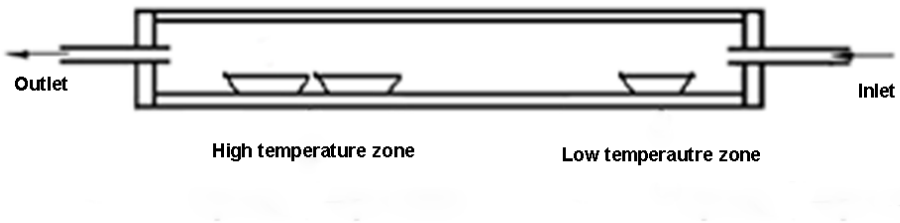

Fig. S1 The boats in the quartz tube

3. AFM image and Layer distribution of the N-doped graphene analogue

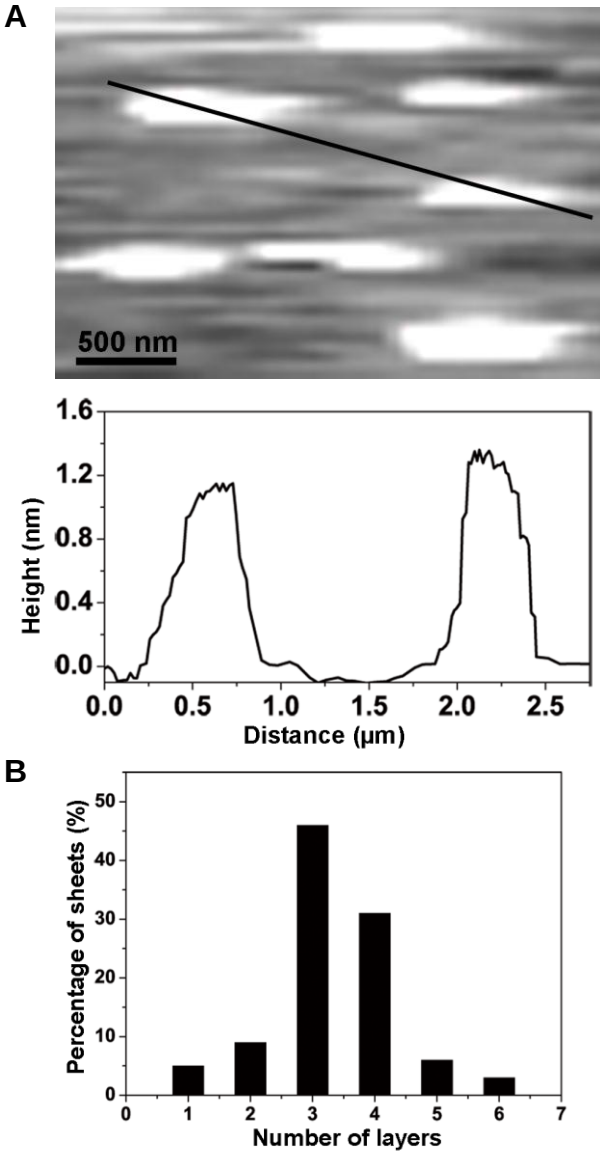

Fig. S2. (A) Typical AFM image and corresponding height profile of the N-doped graphene analogue, (B) layer distribution of the N-doped graphene analogue.

Typical atomic force microscopy (AFM) image with the corresponding height profiles shows the thickness of the N-doped graphene analogue to be 1.15 nm, corresponding to 3 layers (as shown in Fig. S2 A). It shows the size is around 500 nm. 100 pieces of the N-doped graphene analogue were used to show its height distributions. Very narrow graphene layer distributions are observed for the N-doped graphene. The bar charts show that the majority of the N-doped graphene analogue possesses 3 and 4 layers, with occasional presence of 2 and 5 layers (as shown in Fig. S2B).

4. XPS spectra of the crude product

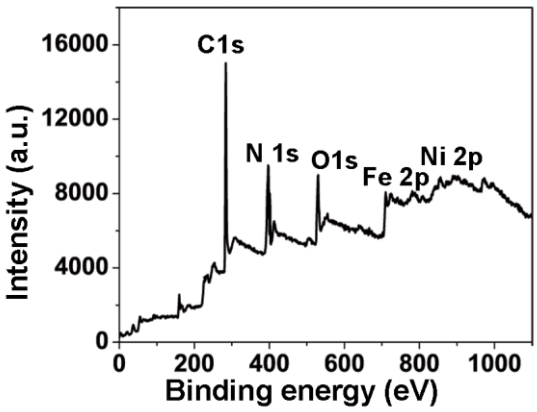

Fig. S3. XPS spectra of the sample before purification

The overall X-ray photoelectron spectroscopy (XPS) spectra shows that the initial crude product obtained consists of C, N, O and a small number of heteroatoms Fe and Ni(Fig. S3). The crude product consists of 71.42% C, 14.33% N, and 9.20 % O, 2.72% Fe and 2.33% Ni by atomic composition.

5. Elemental analysis

The elemental analysis (C, H, N) of the product shows that the weight ratio of C, H and N elements of the obtained N doped graphene are 70.32%, 2.23%, and 16.31%, respectively. The mass percentage of C and N of XPS analysis is slightly larger than that from the elemental analysis results. This is because hydrogen element was excluded in the XPS analysis result.

6. Thermal analysis data

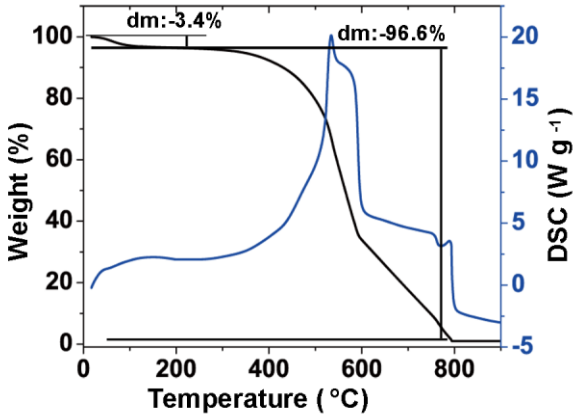

Fig. S4. TG–DSC curves of the N-doped graphene analogue.

Thermal gravimetric analysis and differential scanning calorimetry analysis (TGA/DSC) was performed on a SDT Q600, TA Instruments DSC–TGA, in air with a heating rate of 10 °C min^{-1}. TG and DSC data show that the initial mass loss of the N-doped graphene analogue is 3.4% around 110 ^{o}C. the exothermal peak around 520 ^{o}C can be assigned to the ignition of N-doped graphene analogue (Fig. S4, blue line), and there is a corresponding 96.6% weight loss in the TG curve (Fig. S4, black line).

7. CVs for ORR at the GC electrodes

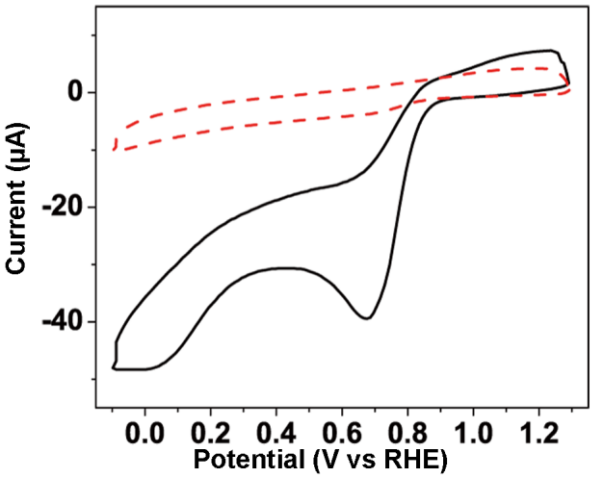

Fig. S5. CVs for ORR at the GC electrodes in nitrogen-protected (dotted curves) or oxygen-saturated 0.1 M KOH (solid curves).

8. Schematic representations of possible adsorption modes of oxygen molecules at the N-doped graphene analogue

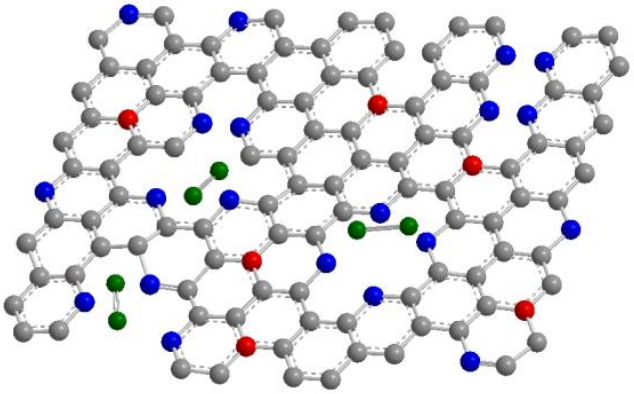

Fig. S6 Schematic representations of possible adsorption modes of oxygen molecules at the N-doped graphene analogue. The blue and red represent "pyridinic" and "graphitic" N atoms in the N-doped graphene analogue, respectively. The green represent O atoms.

References

1. Z. W. Xu, G. X. Zhang, Z. Y. Cao, J. S. Zhao and H. J. Li, *J Mol Catal a-Chem*, 2010, **318,** 101-105.