Supporting Information
Synthesis of hybrid graphene carbon-coated nanocatalysts

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1. Chemical structure of FeTAP

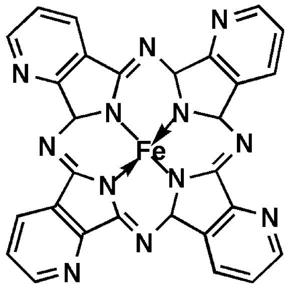

Fig. S1 Structure of FeTAP.

2. Materials and Reagents

pyridine-2,3-dicarboxylic acid (97.0%) and Nafion solution (5 wt% in ethanol) were obtained from Alfa Aesar Co., and all other reagents are of analytical grade and used without further purification.

3. Synthesis of FeTAP

FeTAP was prepared by microwave reaction.[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 ^{o}C; IR (KBr pellet, cm^{-1}): 1664 (s), 1584 (s), 1515 (m), 1105 (s), 924 (m), 794 (s), 753 (s); UV/Vis (DMSO): λ_{max}=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.

4. Characterization

The morphology of the obtained product was characterized by SEM (ZEISS-SUPRA55). The microstructure of the samples was characterized by TEM (JEOL, JEM-3010, 300 kV), and EDS attached to the JEM-3010. Raman spectroscopy was performed with a Renishan InVia system utilizing a 514.5 nm Ar laser, resulting in an approximately 2 μm diameter sampling cross-section. Elemental analysis (carbon, hydrogen, nitrogen) was performed on a Germany VarioEL III CHNOS analyzer. The X-ray photoelectron spectroscopy spectra were recorded by a Kratos AXILS ULTRA spectrometer with Al (Mono) Kα X-ray source (1486.6 eV). AFM measurements were performed using a PicoPlus instrument.

5. Electrocatalytic Performance Tests

Electrochemical experiments were performed by a CorrTest electrochemical work station (CS310 Wuhan CorrTest Instrument Co. Ltd.) in a conventional three-electrode cell using the modified glassy carbon electrode (3 mm diameter) as the working electrode, platinum foil as the auxiliary electrode, and Ag/AgCl as reference electrode. Prior to modification, the glassy carbon electrode was polished with ~ 0.5 μm alumina slurry, washed ultrasonically in distilled water for 3 min and in acetone for 3 min. Sequentially, the cleaned glassy carbon electrode was dried in air. 10 μL of a 2mg mL^{-1} obtained GCC (ethanol) suspension was pipetted onto the glassy carbon electrode. After evaporation of ethanol, 10 µL of a diluted Nafion solution (5 wt% in ethanol) was put on top of the product suspension, and then dried in air. The thin-film electrode was put in an electrochemical cell and immersed in 0.1 M KOH solution for electrochemical measurement. All the experiments were completed at room temperature. The CVs of the glassy carbon electrode is measured by similar method.

6. Magnetic Property Analysis

Magnetic properties of the GCC were investigated at room temperature using a vibrating sample magnetometer with an applied field of -10000 ~ 10000 Gs, to obtain the hysteresis loop of the GCC at room temperature.

7. Thermal analysis data

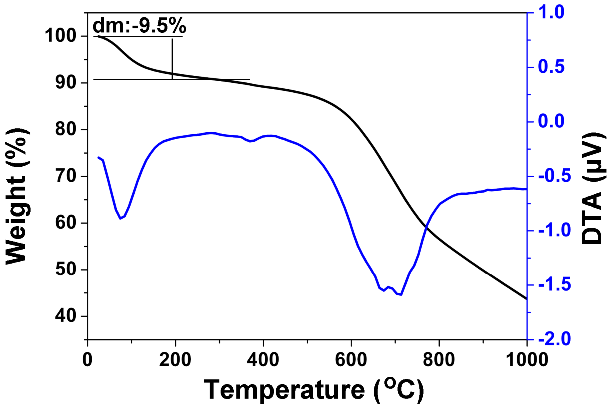

Fig. S2 TG (black) and DTA (blue) data of the obtained GCCs.

TG and DTA data show that the initial mass loss of the obtained GCC is ~9.5% at ~100 °C, indicating the loss of water using as solvent.

8. Elemental analysis and X-ray photoelectron spectroscopic analysis

The component analysis (C, H, N) of the product shows that the weight of C, H and N elements of the obtained sample are 51.03 %, 3.08%, and 3.65%.

The overall XPS spectrum of the obtained GECs shows that the surface of the GECs consists of C and a number of heteroatom N, O and Fe. The atomic ratios of C, N, O, and Fe are 66.70%, 4.10%, 24.30% and 4.90%, respectively (or 52.66% C, 3.78% N, 25.56% O and 18.00% Fe by mass, as shown in Figure 2A). The ratios of C and N are slightly larger than the elemental analysis results. This is because hydrogen element was excluded in the XPS analysis result. The combination results of elemental and XPS analysis indicate the obtained sample is composed of 51.03% C, 3.08% H, 3.65% N, 24.77% O and 17.44% Fe by mass and the atomic ratio of O, H is 1:2. The strong oxygen signal in Fig. 4a was attributed to the adsorbed substances on the sample surface, such as water used as solvent. [2, 3] The C 1s peak at 284.1eV indicates a typical graphite structure (as shown in Fig. S2b). In the Fe 2p spectrum, the peak at 706.1 eV can be assigned as Fe 2p 1/2, while the response of Fe 2p 3/2 is in the position of 720.2 eV (as shown in Fig. S2c). N 1s XPS spectrum of the GECs has one strong peak at 401.2 eV and a shoulder at 398.6 eV, showing that characteristic nitrogen atoms are incorporated into the graphene network (as shown in Fig. S 2d).[3, 4]

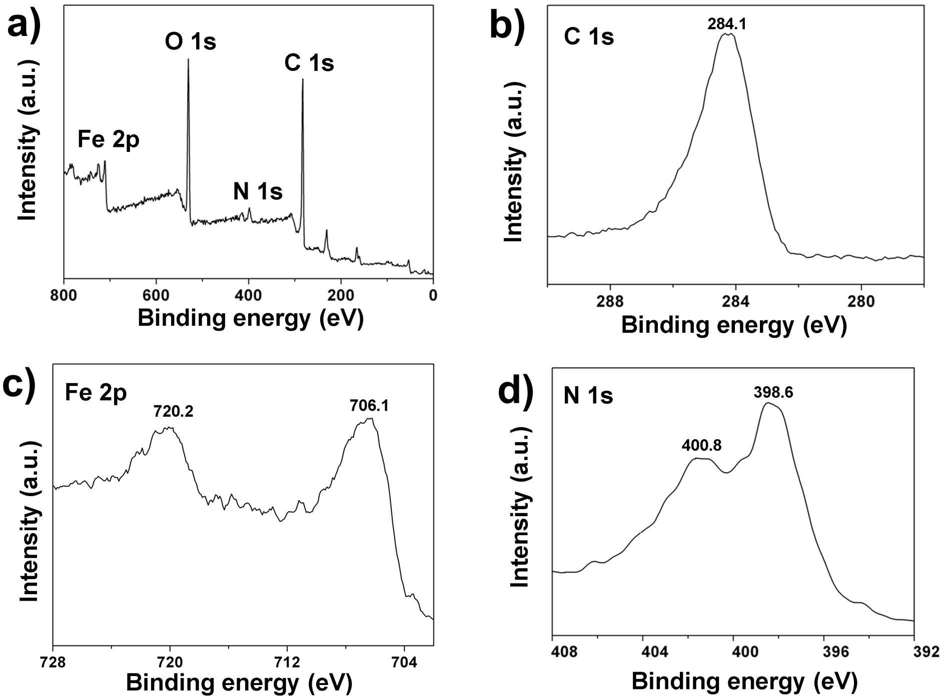

Fig. S3 (a) overall XPS, (b) C 1s, (c) Fe 2p and (d) N 1s XPS spectra of the obtained GCCs.

9. AFM measurements

The graphene can be seperated from the carbon cages by a strong ultrasonic vibration in ethanol solution. Typical atomic force microscopy (AFM) images with the corresponding height profiles show the thickness of the graphene to be about 1.70 nm, corresponding to 5 layers (Fig. S4).

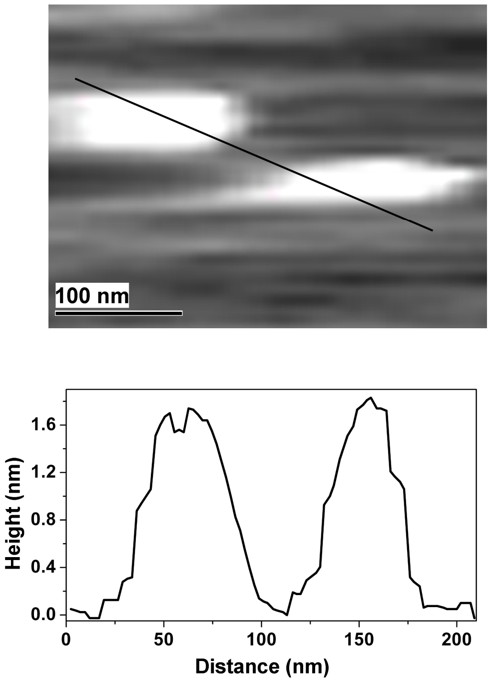

Fig. S4 Typical AFM images and corresponding height profile of the graphene.

10. Influence of the synthesis time on the size of the product particles

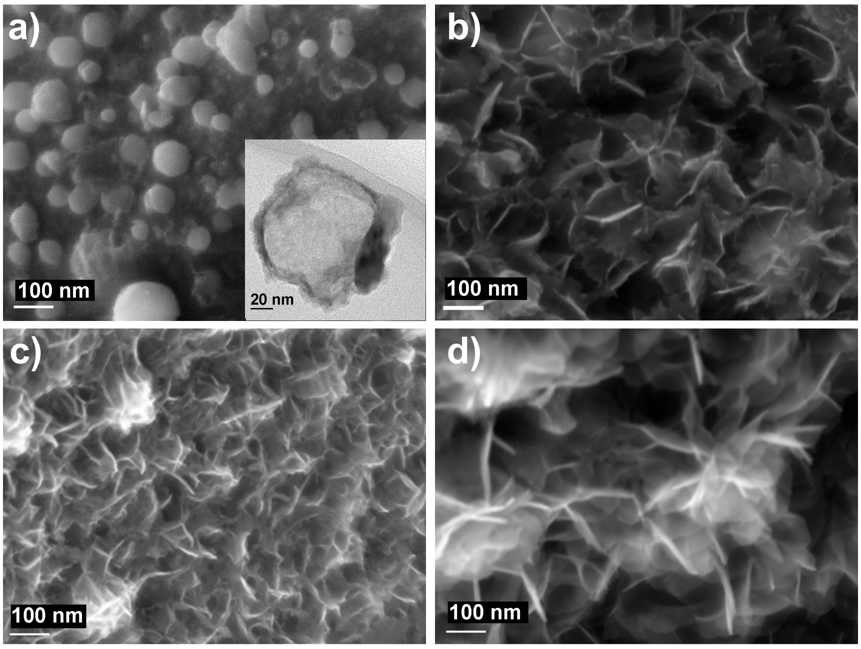

Fig. S5 SEM images of the products by prolysis of FeTAP at 950 °C for 40 (a) (the inset is TEM image of the product), 120 (b), 80 (c) and 160 min (d).

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