

## *Electronic Supplementary Information*

### **Electrocatalytic Reduction of Trace Nitrobenzene Using Graphene-Oxide@Polymerized-Manganese-Porphyrin Composite**

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#### **Synthesis of 5,10,15,20-Tetra(4-nitrophenyl)porphyrin (TNPP)**

A solution of nitrobenzene (25 mL) and lactic acid (7 mL) was heated up to backflow, then added nitrobenzene (12 mL) which was mixed with distilled pyrrole (27.5 mmol, 1.84 g) and p-nitrobenzaldehyde (27.5 mmol, 4.00 g) in 20 min. The mixture solution was stirred at 135 °C for 2 h, cooled to 60 °C and injected methyl alcohol (15 mL), the sediment was collected by filtration and washed with methyl alcohol for three times. The product was dried at 60 °C in vacuum to gained crystalline purple powder TNPP.

#### **Synthesis of 5,10,15,20-Tetra(4-Aminophenyl)Porphyrin (TAPP)**

At room temperature, TNPP (2.05 mmol, 1.65 g) and concentrated hydrochloric acid (75 mL) were added together, then SnCl<sub>2</sub>·2H<sub>2</sub>O (29 mmol, 7.00 g) dissolved in concentrated hydrochloric acid (20 mL) was drop slowly to the solution in 10 min. The mixture was stirred at room temperature for 2.5 h. Then heated the mixture up to 65-70 °C and stirred for 30 min. Cooled to room temperature and collected the crude product by filtration, added the crude product to deionized water (200 mL) and adjusted the pH to 9 with stronger ammonia water, gained the precipitate by filtration. The product was further purified by Soxhlet extraction with chloroform and collected the product by rotary evaporation. The product was dried at 60 °C in vacuum to gained atropurpureus powder TAPP.

#### **Synthesis of Mn(II)[5,10,15,20-tetra(4-aminophenyl)porphyrin] (MnTAPP)**

A mixture solution of TAPP (0.3315 g, 0.33 mmol) and MnCl<sub>2</sub>·4H<sub>2</sub>O (2.0 g, 10mmol) in DMF (60 mL) was added into a 100 mL flask, heated it up to reflux temperature (145 °C). The mixture solution was stirred for 2 h at 145 °C, cooled to room temperature and pured into deionized water (60 mL), adjust the PH to 9-10 by ammonium hydroxide, some precipitate would separate out. The precipitate was collected by filtration and washed by water until the filtrate was achromatic color, used the aluminium oxide (100-200 mesh) chromatographic column

(chloroform/methanol, 5:1) to further purified the crude product, The product was dried at 60 °C in vacuum to gained atropurpureus powder MnTAPP.

### Synthesis of grapheme oxide (GO)

The GO is prepared by the Hummer method. The specific steps are as follows: (1) synthesis graphite oxide, adding concentrated sulfuric acid (23 mL) to a 250 mL three-necked flask, placing it in an ice water bath for cooling, and then adding phosphorus graphite(1 g ) and nitric acid (0.5 g). Mix the sodium, stir for 30 min; then slowly add potassium permanganate (3 g) in several times, the solution becomes dark green viscous, react for 2 h, heat up to 38 °C by heating in water bath, stir for 30 min, slowly add 120 mL of deionized water, The solution turns brownish yellow, the temperature rises to about 90 °C, then the temperature drops with the addition of deionized water, then the oil bath is heated to 98 °C, after half an hour of reaction, add a little H<sub>2</sub>O<sub>2</sub> with a mass fraction of 30%, the unreacted potassium permanganate was removed, and the solution turned bright yellow. It was then poured into a 1000 mL large beaker and diluted with a large amount of deionized water. (2) Synthesis graphene oxide, the obtained graphite oxide diluted solution was ultrasonicated for about 2 h to obtain a dispersion of graphene oxide. Separately with 5% hydrochloric acid solution, deionized water to remove Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, and then dried at 60 °C in vacuum for 24 h to obtain graphene oxide(GO).

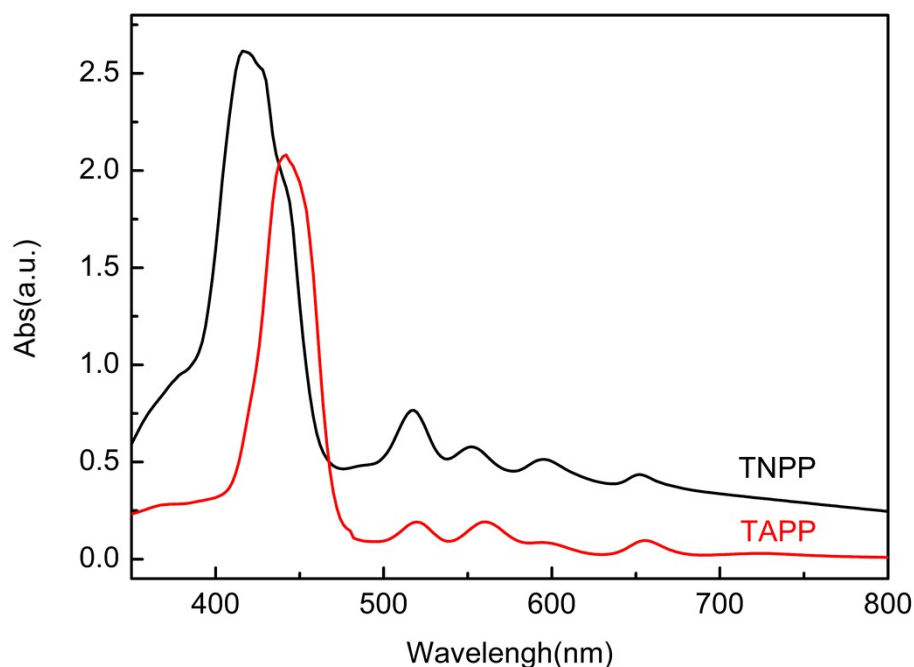


Fig.S1 UV-Vis spectra of TNPP and TAPP in DMF.

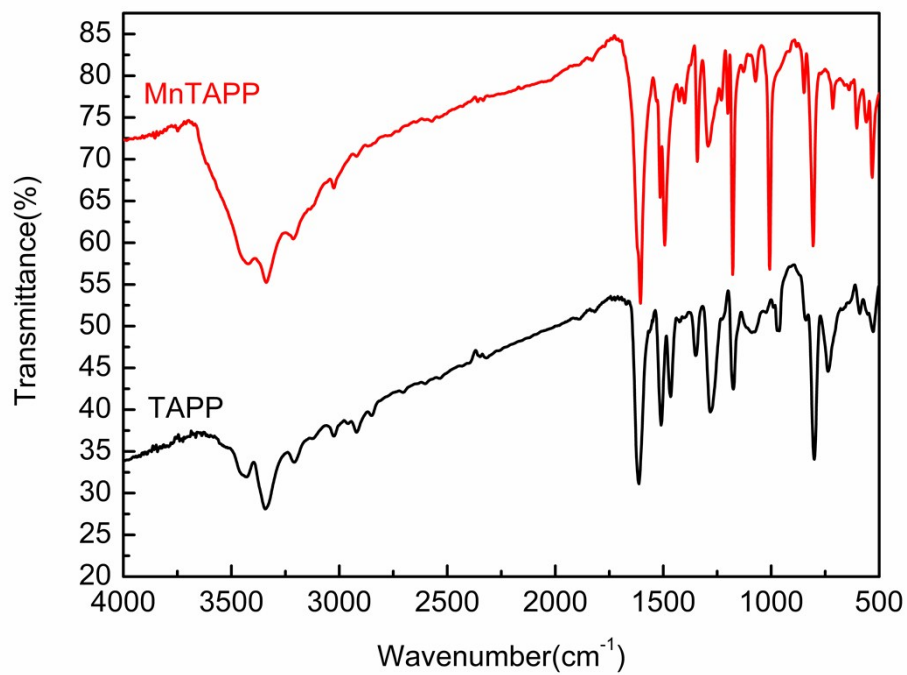


Fig. S2 FT-IR spectra of TAPP and MnTAPP.

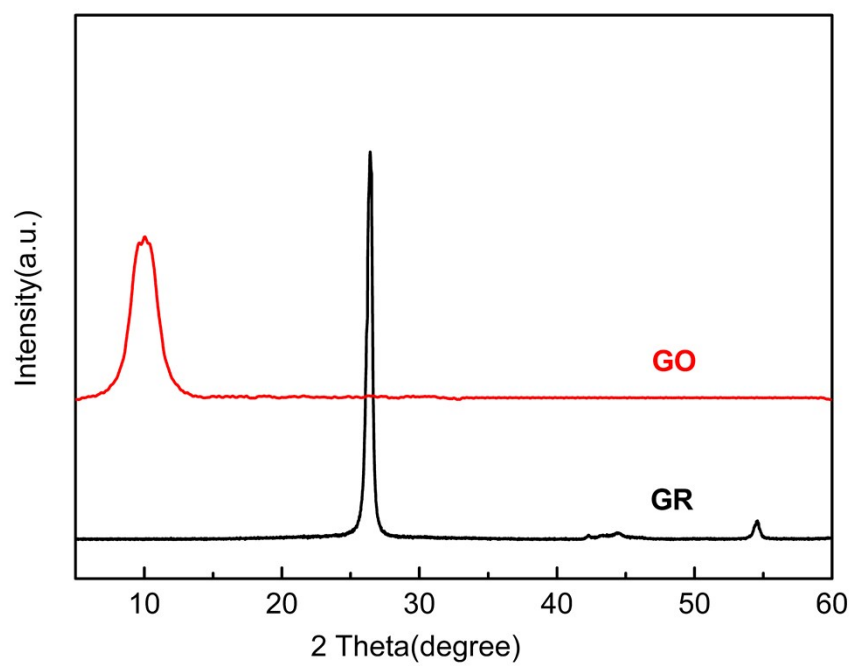
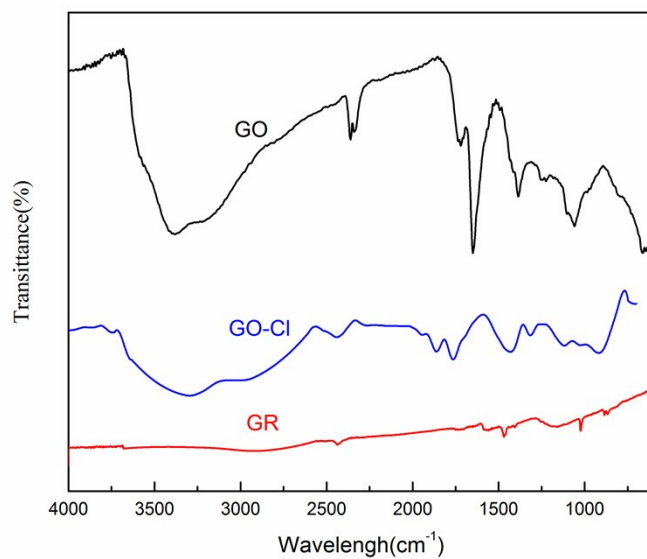
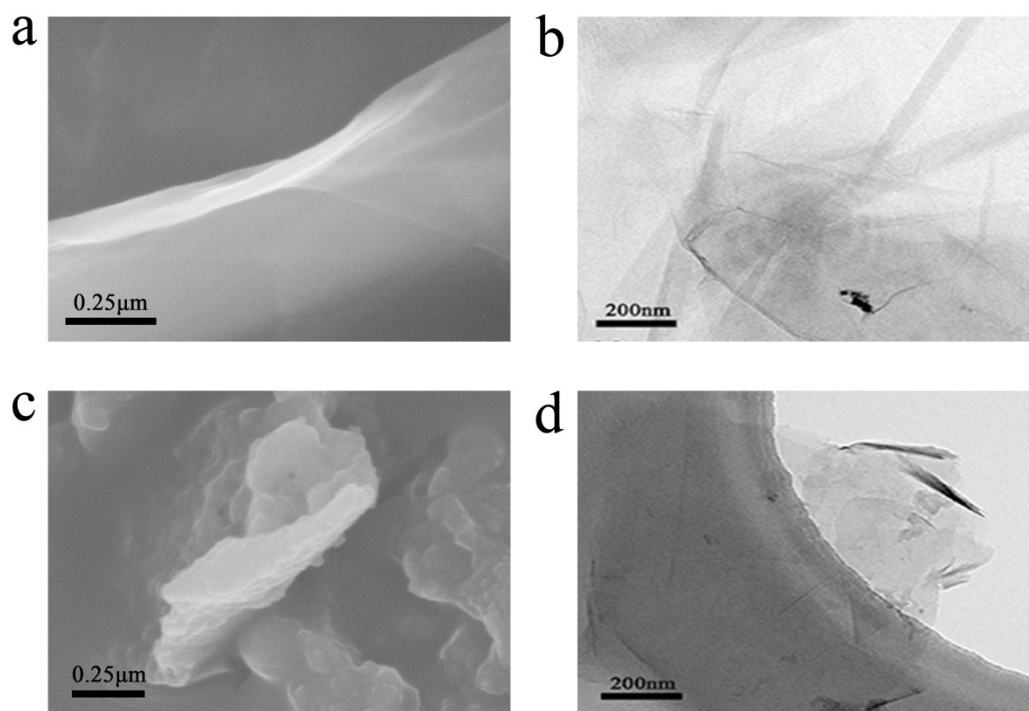


Fig. S3 XRD pattern of GR and GO.



**Fig. S4** FT-IR spectra of GR , GO.and GO-Cl.



**Fig. S5** (a) SEM and (b) TEM of GO; (c) SEM and (d) TEM of GO-MnTAPP.

**Table S1** The current value of the DPV curve of the blank sample (0.5M NaCl standard solution without nitrobenzene) at -0.75V

Experiment number	1	2	3	4	5
Peak current ( $\mu\text{A}$ )	-13.611	-13.353	-13.334	-13.262	-13.394
Experiment number	6	7	8	9	10
Peak current ( $\mu\text{A}$ )	-13.616	-14.020	-13.657	-13.464	-13.269

**Table S2** Peak current value of DPV curve in 0.5M NaCl solution with GMPP@AMP/GCE as working electrode

Experiment number	1	2	3	4	5
Peak Current ( $\mu\text{A}$ )	-141.432	-141.011	-141.363	-141.583	-141.296
Experiment number	6	7	8	9	10
Peak Current ( $\mu\text{A}$ )	-141.286	-141.069	-141.369	-141.356	-141.034

**Table S3** NB recovery studies in real water samples (n=3)

Sample	Addition amount ( $\mu\text{M}$ )	Detection Quantity ( $\mu\text{M}$ )	Recovery (%)
Runing Water	50	48.3	96.6
	100	97.7	97.7
	150	147.9	98.6
	200	189.3	94.65