

Electronic Supplementary Information

1. Preparation of CA-cMWCNTs

Carboxylated multiwall carbon nanotubes (**cMWCNTs -COOH**) was purchased from Shenzhen Nanotech Port Co., Ltd., China (purity: > 97%, length: < 5 μm , diameter: 20 – 40 nm, the carbon atom bearing OH group: 3.0 %, the carbon atom bearing COOH group: 2.3%)

Under supersonification, **cMWCNTs-COOH** (0.67g), was dispersed in the mixture of SOCl_2 (0.8 mL), DMF (3 drops) and THF (8 ml) and refluxed for 24 h at 65 °C. Then, the solvent was removed under reduced pressure. To fully remove the residual SOCl_2 , the products were repeatedly dispersed in THF and separated *via* centrifugation (10000 rpm, 10 min). To the newly **cMWCNTs-COCl** was added a solution of **CA** (0.6 g) in THF (15 ml) and pyridine (0.8 ml) under vigorous stirring. The mixture was refluxed for 6 h. Then the solvent was removed under vacuum and the residual washed with water by 6 times to remove the excess pyridine and its salt form.

2. Preparation of the electrospun-fibre membranes

CA, **Fe₂** and **PVP** were dissolved in a mixture of acetone/DMAc (V/V = 1:1) and then **CA-cMWCNTs** was added under constant stirring at room temperature for about 8 h.

The detailed percentage of these gradients of an electrospinning composite was shown in Table S1. For electrospinning, the solution (5.0 mL) was loaded in a glass syringe with a stainless steel pin jointed in the solution and connected to a power supply (JG50-1, Shanghai Shenfa Detecting Instrument Factory, China), which was docked to a syringe pump (KDS200, KD Scientific Inc., USA) with a steady flow rate of 1.5 mL h⁻¹. Grounded counter electrode was connected to a stainless steel collector ($S = 15.2 \text{ cm}^2$) that was 15 cm away from the spinneret which was perpendicular to the collector in a coaxial manner. The electrospinning was performed under voltages 9.7 kV at room temperature and humidity between 73-82%. Electrospinning time of 15 min was employed unless otherwise stated. The resulting fibrous mats were collected and dried under vacuum at room temperature for 10 h.

Table S1 Composition of the electrospinning solution

Gradient	Acetone	DMAc	PVP	CA	CA-CNT	Fe ₂
Volume or weight	2.2 ml	1.1 ml	0.11 g	0.31 g	0.025 g	0.17 g
% ^a			17.9%	52.1%	2%	28%

^aThe solvent (acetone and DMAc) was excluded in calculating the percentage of the composite.

3. Electrochemistry set-up

Electrochemical investigations were carried out in a conventional three-electrode

system under an N₂ atmosphere and electrochemical data were collected using Autolab 128N (Metrohm, Netherland). KCl solution (0.1 mol L⁻¹) was used as supporting electrolyte. The reference electrode was Ag/AgCl in KCl (saturated solution) electrode while the auxiliary electrode was a platinum wire.

4. Figures



Fig. S1 CA-cMWCNTs (left) and a mechanic mixture of CA and cMWCNTs (right) in DMAc after half a month's standing.

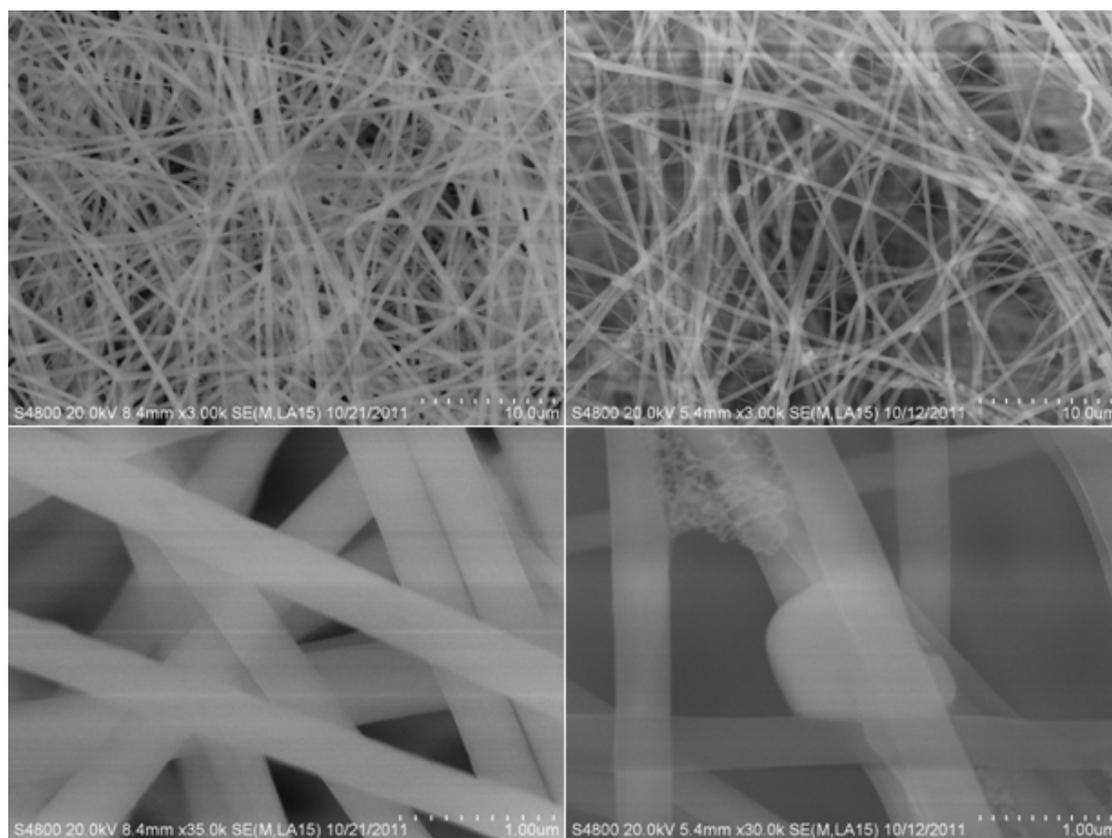


Fig. S2 SEM images of the electrospun-fibers membrane **EFM-Fe₂** before (left) and after (right) electrochemistry. Please note that residual KCl crystals are seen among the fibers after electrochemistry.

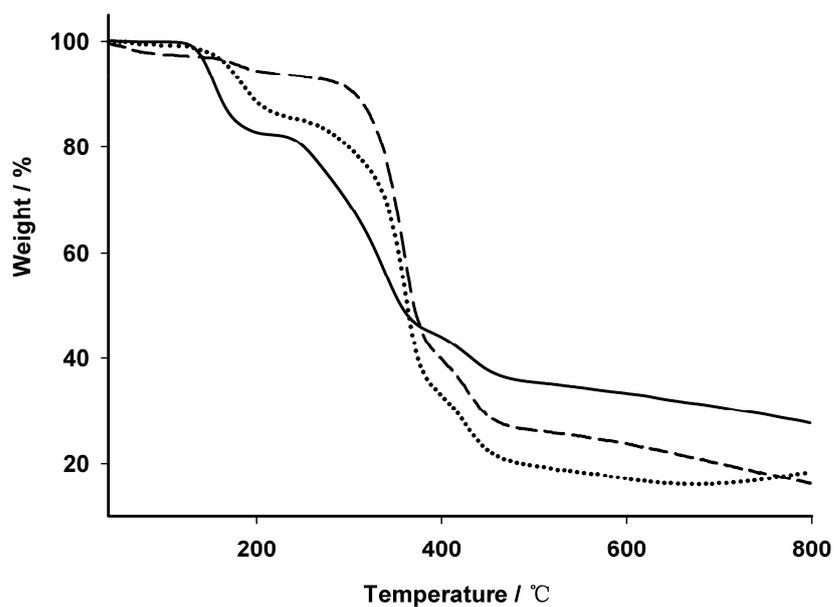


Fig. S3 TGA traces of the electrospun-fibers membranes of **EFM-Fe₂** (solid line), **CA+PVP** (dot line), and **CA-cMWCNTs+PVP** (dash line).

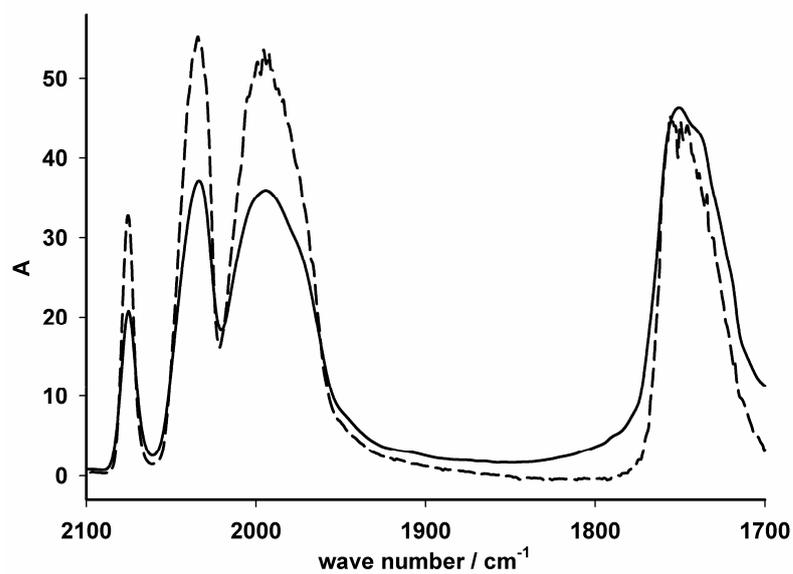


Fig. S4 Infrared spectrum of **EFM-Fe₂** before (dash line) and after (solid line) electrochemistry (150 repetitive scans).

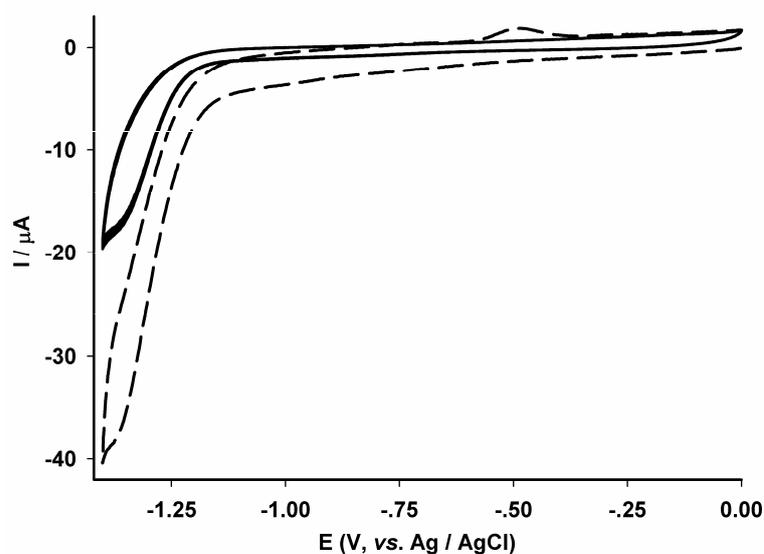


Fig. S5 Cyclic voltammograms of **EFM-Fe₂** at the first scan (dash line) and the 150th scan (solid line) in 0.1 mol L⁻¹ KCl / H₂O.

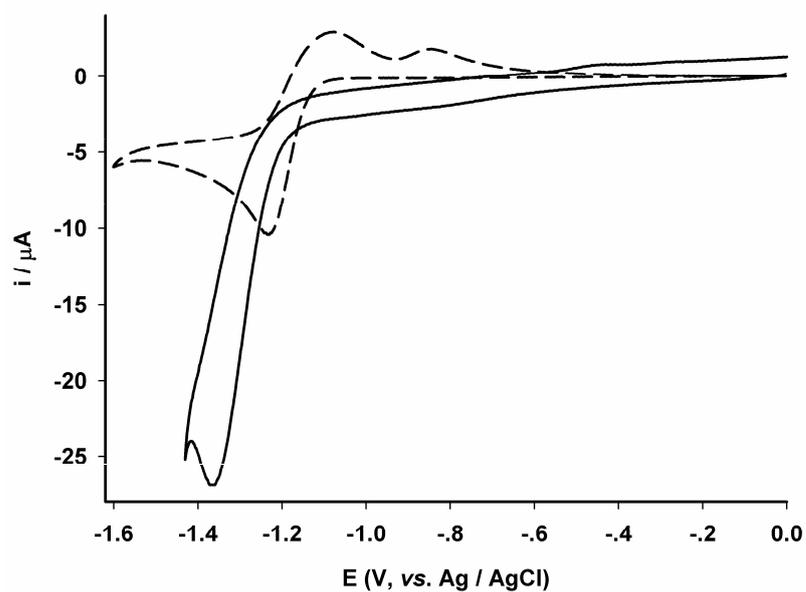


Fig. S6 Cyclic voltammograms of complex **Fe₂** (dash line, vitreous carbon electrode, $\phi = 1\text{ mm}$, $C = 5\text{ mmol L}^{-1}$) in 0.1 mol L⁻¹ [NBu₄]BF₄ / MeCN, **EFM-Fe₂** membrane electrode (solid line, $\phi = 5\text{ mm}$) in 0.1 mol L⁻¹ KCl / H₂O; (3.5 mL, room temperature, scanning rate = 0.1 V / s⁻¹).