

Supporting information:

Rapid capture of Ponceau S via a hierarchical organic-inorganic hybrid nanofibrous membrane

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Experimental details

Materials:

Polyacrylonitrile (PAN $M_w = 90,000$) was purchased from Kaneka Co., Ltd., Japan. Dimethylacetamide (DMAc) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were supplied by Shanghai Aladdin Chemical Co., Ltd., China. Polyethyleneimine (PEI $M_w = 600$), dopamine (DA) and Tris-HCl were purchased from Shanghai Richjiont Chemical Reagents Co., Ltd., China. Ponceau S was purchased from Beijing biotechnology development center Ltd., China. Pure water was obtained from a Millipore system. All chemicals were of analytical grade and were used as received without further purification.

Preparation of FeCNF membranes

The electrospun FeCNFs were fabricated as follows. The precursor solution was prepared by dissolving 0, 0.5, 1.5 and 2.5 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 45 g DMAc at room temperature with vigorous stirring for 1 h, then added 5 g of PAN with vigorous stirring for 12 h. Following, the hybrid solution was vigorously stirred for 6 h at 60 °C until a viscous solution of the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ /PAN was obtained. The electrospinning process was performed at a fixed high voltage of 30 kV and a controllable feed rate of 1.0 mL h⁻¹ with a distance of 20 cm between the needle tip to the round collector. The relevant temperature and humidity during electrospinning were 23±2 °C and 42±3%. The green body of fibrous membrane was collected on the aluminum foil. The green body was calcined at 850 °C in N₂ flow to form hybrid carbon nanofibrous membrane. Different concentrations of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ /PAN solution are denoted as FeCNFX in the subsequent discussion, where X stands for the concentration of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The weight percentage of iron in $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is 13.86% and the weight percentage of carbon in PAN is 67.92%. For FeCNF50, therefore, the weight ratio of Fe to C in the electrospun solution is $50 \times 13.86\% : 100 \times 67.92\% = 1:9.8$.

Surface modification of FeCNF membrane with dopamine and PEI

FeCNFs were modified with aqueous solutions of dopamine (2 mg ml⁻¹) and PEI (6 mg ml⁻¹) in 10 Mm Tris-buffer, pH=8.5 .The pH value of solution was monitored with pH meter (Mettler Toledo FE-20). The PEI/dopamine solution was stirred at room temperature for 24 h. The FeCNF coated with PDA/PEI were suction filtered, rinsed thoroughly with deionized water at least three times, and dried in a vacuum oven at 50 °C for 12 h.

Adsorption measurement

For the adsorption experiments, an aqueous solution of negative Ponceau s was chosen as the typical contaminant organic dye wastewater. Generally, 20 mg of FeCNF and PDA/PEI coated FeCNF were immersed into 15 mL of test aqueous solution (5 ppm) with string for a designated time, which was measured by UV-Vis spectra to measure the resultant adsorption capacity at certain time intervals. C_t/C_0 was used to evaluate the adsorption rate. Where C_0 (mg/L) and C_t (mg/L) are the initial concentration and the concentration at time t , respectively. During the cycling test of absorbent, the CNF membranes were transferred into NaOH solution (0.5mol/L) for 15 min to elute the adsorbent dye then washed by deionized water and ethanol for at least three times until the washing solution reach neutral.

Characterizations

The morphology of NFMs was examined by a scanning electron microscope (SEM, Zeiss SUPRA 55 SAPPHIRE) equipped with an energy-dispersion X-ray spectrometer (EDS, Oxford X-max) at acceleration voltages of 2 kV and 20 kV, respectively. High resolution picture and selected area electron diffraction patterns of CNFs were obtained by transmission electron microscope (JEM-2100F, JEOL Ltd.) at an acceleration voltage of 200 kV. Crystal structure of CNFs was measured by X-ray diffractometer (XRD, Rigku, ultima IV) using a Cu K α (0.154 nm) radiation under the conditions of 40 mA and 40 kV. The textural properties such as surface area (BET, DFT) and pore size distribution of the samples were derived from N₂ adsorption–

desorption measurements carried out at -196 °C using an automatic micropore physisorption analyzer (Tristar 3020, USA) after the samples were degassed at 300 °C for at least 10 h under 0.133 Pascal pressure prior to each run. Thermal degradation measurements were performed at a Thermogravimetric analysis (TGA) (NETZSCH, STA 449F3). The near-surface chemical information of materials were analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha, Al K α radiation, 1486.6 eV, 12 kV, 3 mA). XPS peak positions were calibrated with the help of the C 1s peak at 285.0 eV. Fourier-transform infrared spectroscopy (FT-IR, Thermo Scientific, Nicolet 6700) was applied to detect the presence of dopamine. Magnetic properties were measured with a vibrating sample magnetometer (VSM, Lake Shore 7304). Raman spectrum was obtained by using a micro-Raman spectroscopy system (inVia-Reflex, Renishaw, Co., UK). The concentration of dye in the treated solution was determined by UV–Vis spectra (Shimadzu UV spectrophotometer, UV-1800).

Figures

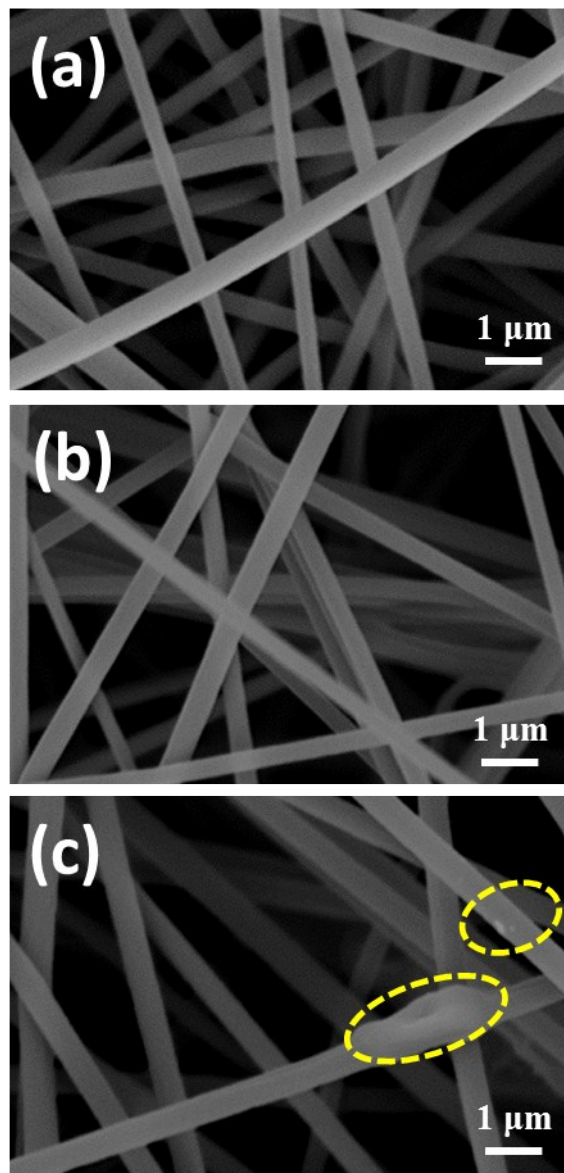


Fig. S1 SEM images of as-electrospun CNFs with different iron contents (a) 0%, (b) 10% and (c) 30%.

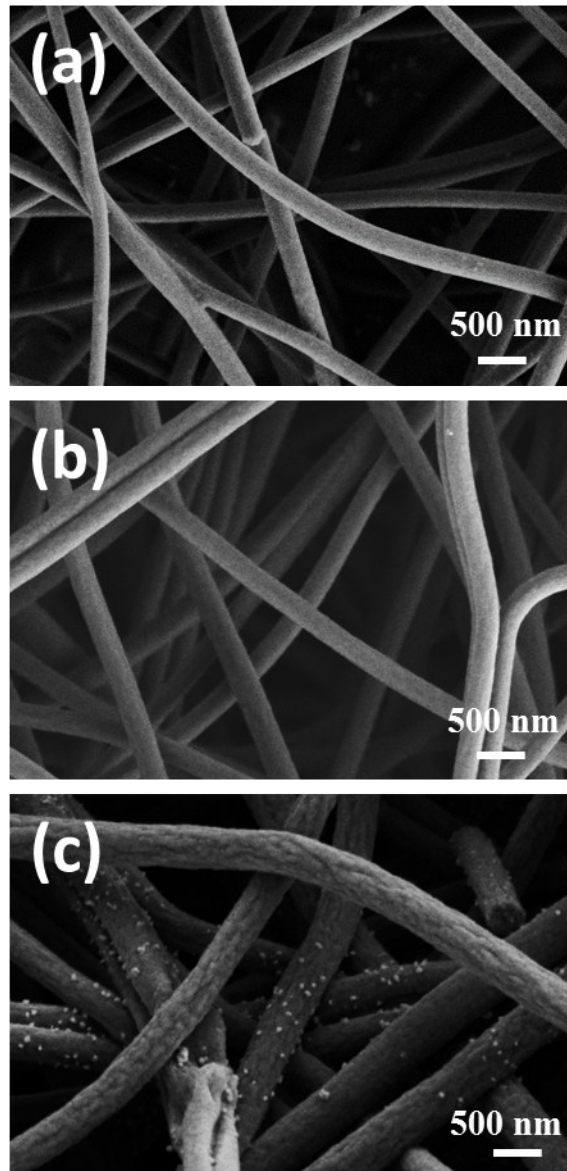


Fig. S2 SEM images of CNFs with different iron contents after calcination (a) 0%, (b) 10% and (c) 30%.

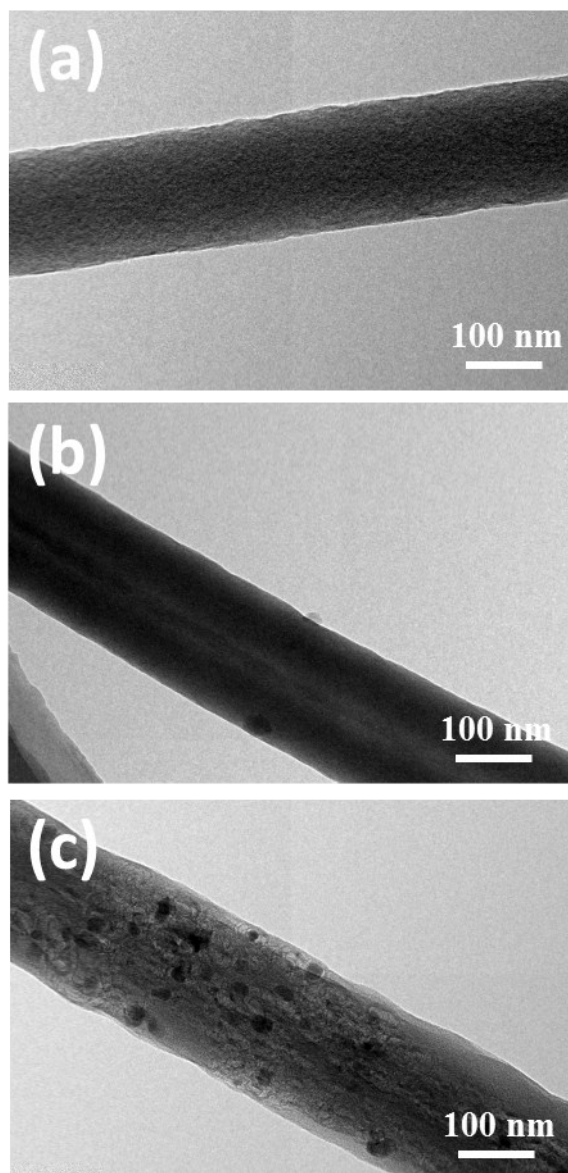


Fig. S3 TEM images of CNFs with different iron contents after calcination (a) 0%, (b) 10% and (c) 30%.

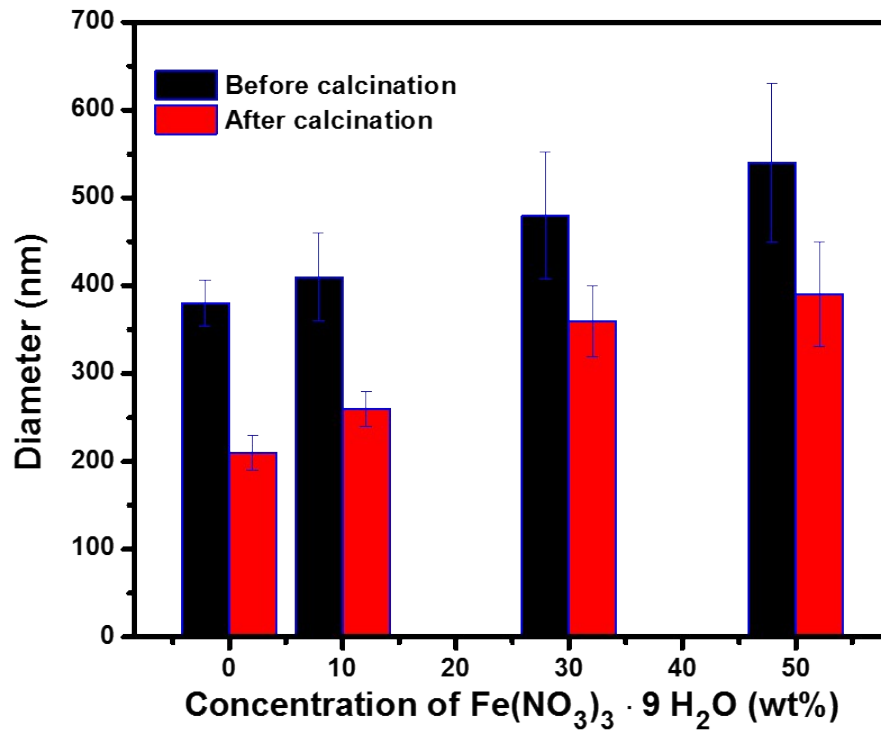


Fig. S4 The relevant precursor fiber diameter before and after calcination with various $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

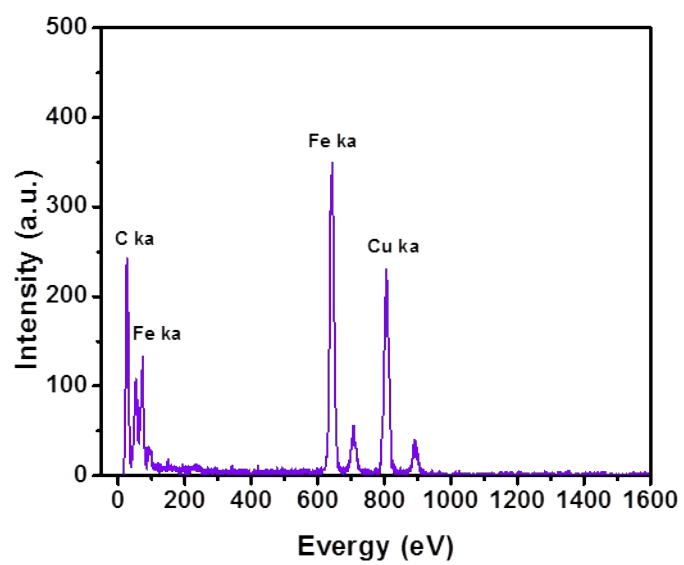
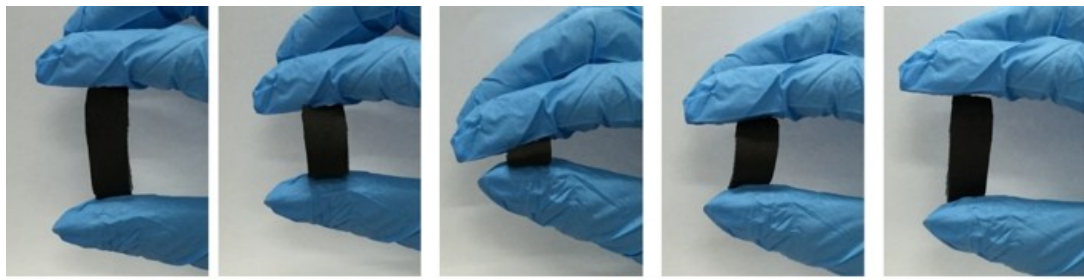


Fig. S5 EDX spectra of a selected area of selected a single fiber.



Bending and recovering

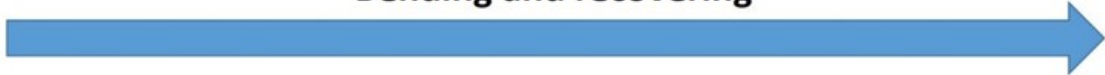


Fig. S6 Picture of bending and recovering demonstration of FeCNF50 membrane.

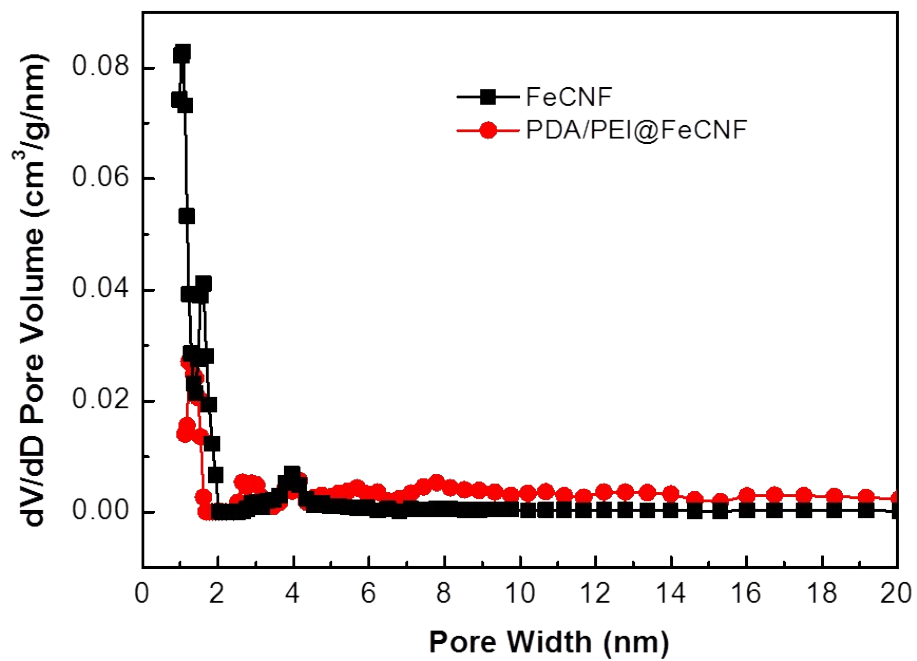


Fig. S7 Pore size distribution of FeCNF50 and PDA/PEI@FeCNF50 by DFT method.

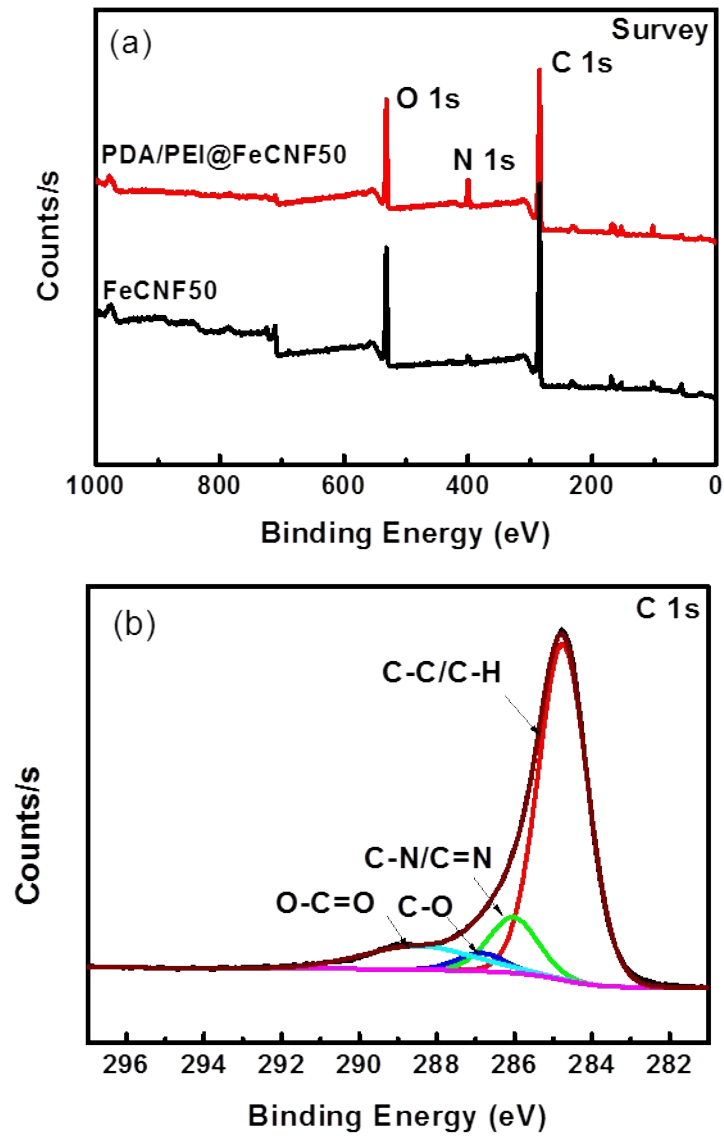


Fig. S8 (a) XPS results of FeCNF50 before and after PDA/PEI coating; (b) C1s spectra of PDA/PEI@FeCNF50.

Table S1 Comparison of the properties of FeCNF50 with the literature results

Name	Prepared method	Surface area (m ² /g)	Type of dye	Response time (min)	Ref.
MgO nanoparticles	Co-precipitation method	22.1	Ponceau S	120	29
ZnO nanoparticles	Co-precipitation method	--	Ponceau S	90	30
PDA/PEI@FeC NF50	Co-electrospin/multi- treatment	73	Ponceau S	20	This work
FeCNF50	Co-electrospin	117	Ponceau S	60	This work