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General strategy for fabricating flexible magnetic silica nanofibrous membranes with multifunctionality

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Support information

Materials

Poly(vinyl alcohol) (PVA, M_w=88000), phosphoric acid (H_3PO_4, 85 wt%), ferric chloride ($FeCl_3$), nickel chloride ($NiCl_2$), and gelatin were purchased from Shanghai Chemical Reagents Co., Ltd., China. Tetraethyl otrhosilicate (TEOS) was purchased from Lingfeng Chemical Co., 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 flexible SNF

The precursor solution was prepared by dissolving the PVA in pure water at 80°C with vigorous stirring for 10 h. The silica sol was generated from the hydrolysis of TEOS by dropwise addition of H_3PO_4 and H_2O with the molar composition of TEOS:H_2O:H_3PO_4:=1:11:0.01. Following, 10 g of resultant silica sol was added to the PVA (10 g) solution and stirred for another 6 h. The electrospinning process was performed by using a DXES-3 spinning equipment (Shanghai Oriental Flying Nanotechnology Co., Ltd., China) with an applied high voltage of 20 kV and a controllable feed rate of 1 mL h^{-1}. The relevant temperature and humidity during electrospinning were 25 ± 2°C and 45 ± 5%. Finally, the composite membranes were calcined to 850°C by gradually increasing the temperature at the heating rate of 5 °C min^{-1} in air to remove the PVA.

Fabrication of $NiFe_2O_4$@SNF

In a typical experiment, 6.13 g of $FeCl_3$ and 1.87 g of $NiCl_2$ (a mole ratio corresponding to the nominal composition of Fe:Ni ratio of 2:1) were dissolved in 92 g of water. 4 g of gelatin is dissolved in 96 g of water under stirring at 70°C. The warm gelatin solution was dropwise added to the metal salts solution under heating and stirring, until a homogeneous mixed gelatin sol was obtained. Subsequently, the SNF was cut into 5 ×

5 cm^2 pieces and dipped in the mixed sol for 5 min. Following, the membranes were dried in the oven at 50^oC for 20 min, and placed in the center of a microwave oven with power of 400 W for 3 min, leading to the formation of the crosslinked gelatin layer on fiber surface which contained embedded $FeCl_3$ and $NiCl_2$ (gelatin/SNF). Finally, the gelatin/SNF was calcined at 750^oC for 30 min with the heating rate of 5 ^oC min^{-1} in N_2 flow (the N_2 flow rate was 0.002 m^3 min^{-1}), and yielded the magnetic $NiFe_2O_4$@SNF.

Magnetic adsorption measurement

The adsorption performance of $NiFe_2O_4$@SNF was tested by the removing of the typical dye pollutants of methylene blue (MB). Generally, 20 mg of $NiFe_2O_4$@SNF was immersed into 20 mL of test aqueous solution (1×10^{-5} M) with string for a designated time, then the UV-Vis spectra (PG2000-Pro, Ideaoptics Technology Ltd., China) were used to measure the resultant adsorption capacity at certain time intervals.

Emulsion separation experiments

To prepare the oil-in-water emulsions, the surfactant (Tween 80, 0.1 wt%) was first dissolved in water, and a certain amount of oil (petroleum ether, 1 wt%) was added into the water. Following, the mixture was emulsified by a high-speed homogenizer (5000 rpm for 5 min) and was further homogenized by an ultrasonic treatment (5 min). The as-prepared $NiFe_2O_4$@SNF with diameter of 40 mm was sandwiched between two vertical glass tubes. The freshly prepared emulsion was poured onto the samples and the water spontaneously permeated. The flux was determined by calculating the volume of oil permeated within 1 min.

Characterization

Field emission scanning electron microscopy (FE-SEM) images and energy-dispersive X-ray spectroscopy images were examined by Hitachi S-4800, Hitachi Ltd., Japan. Transmission electron microscopy images and selected-area electron diffraction patterns were measured by using JEM-2100F, JEOL Ltd., Japan. FT-IR spectra were performed with a Nicolet 8700 FT-IR spectrometer in the range 4000-400 cm^{-1}. The phase structure was characterized with X-ray diffraction (D/Max-2550 PC Rigaku Co., Japan). Magnetic properties were measured with a vibrating sample magnetometer (VSM, Lake Shore 7304, USA). N_2 adsorption-desorption isotherms and BET surface areas were examined at 77 K by an ASAP 2020 physisorption analyzer (Micromeritics Co., USA). Water contact angle (3 μL) and oil contact angle (3 μL) measurements were performed by a contact angle goniometer Kino SL200B equipped with tilting base. The mechanical properties of the membranes were measured on a tensile tester (XQ-1C, Shanghai New Fiber Instrument Co., Ltd., China).

Structure confirmation of $NiFe_2O_4$@SNF by FT-IR and XRD analyses.

Evidence for the formation of crosslinked gelatin layer on SNF surface came from FT-IR spectral analysis (Fig. 3a), the characteristic peak around 3400 cm^{-1} was assigned to the N-H stretching vibration, and the peaks around 1647 cm^{-1} belonged to the C=O stretching vibration of amide groups. The corresponding selected-area electron diffraction (SAED) pattern (Fig. 2i) of $NiFe_2O_4$@SNF showed spotty ring patterns without any additional diffraction spots and rings of second phases, revealing the crystalline spinel structure of $NiFe_2O_4$ NPs. In combination with the X-ray diffraction (XRD) presented in Fig. 3b, the relevant lattice planes of 30.4^{o} (220), 35.8° (311), 37.4° (222), 43.4° (400), 57.4° (511), and 63.1° (440) are consistent with the standard XRD data for the $NiFe_2O_4$ phase (JPPDS No. 10-0325).

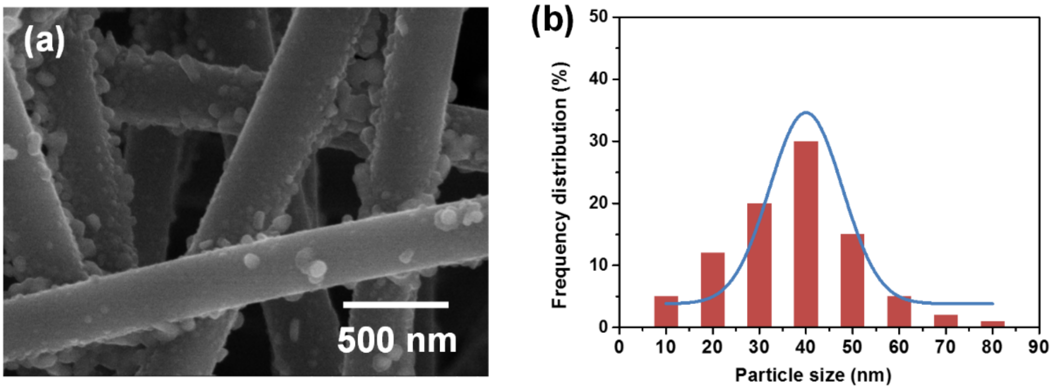

Fig. S1 (a) FE-SEM image showed that the $NiFe_2O_4$ NPs were well located on the fiber surface. (b) Histogram showing the particle size distribution of the $NiFe_2O_4$ NPs.

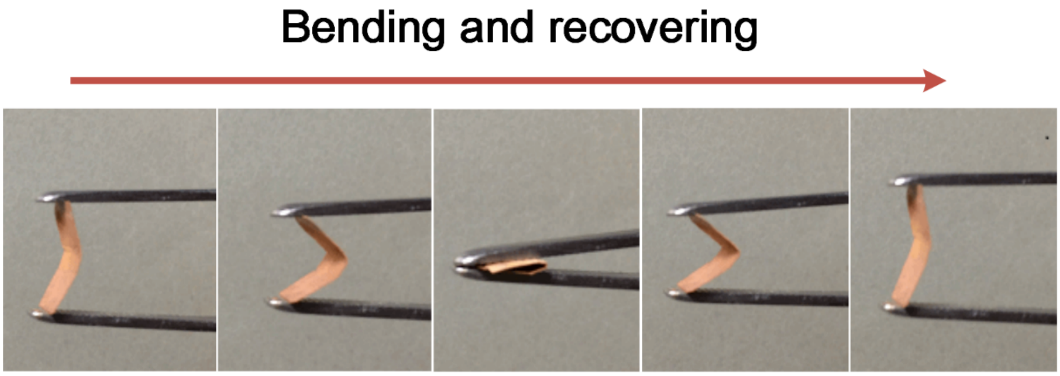

Fig. S2 Optical images presenting the flexibility of $NiFe_2O_4$@SNF by facilely bending and recovering.

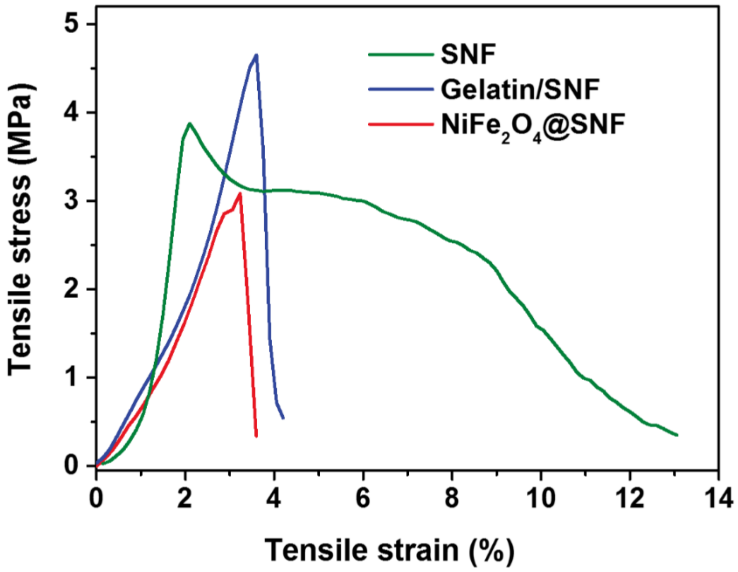

Fig. S3 Stress-strain curves of SNF, gelatin/SNF, and $NiFe_2O_4$@SNF.

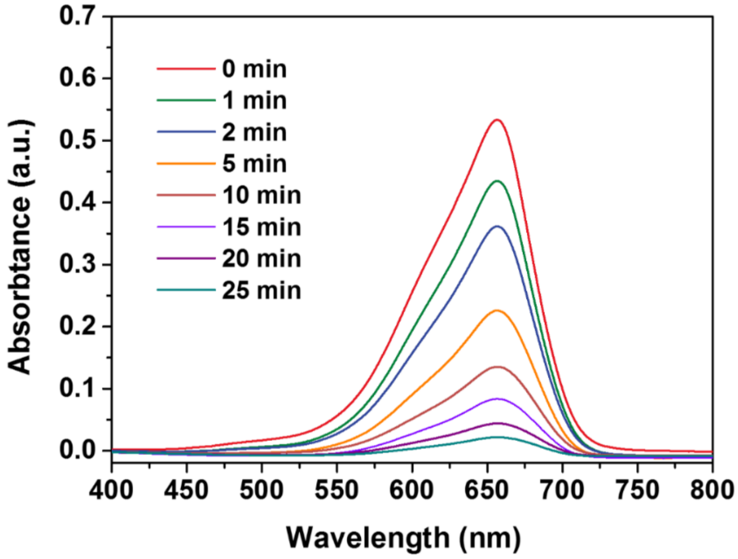

Fig. S4 UV-Vis spectra of MB solution (1×10^{-5} M) after treatment with $NiFe_2O_4$@SNF for various time.

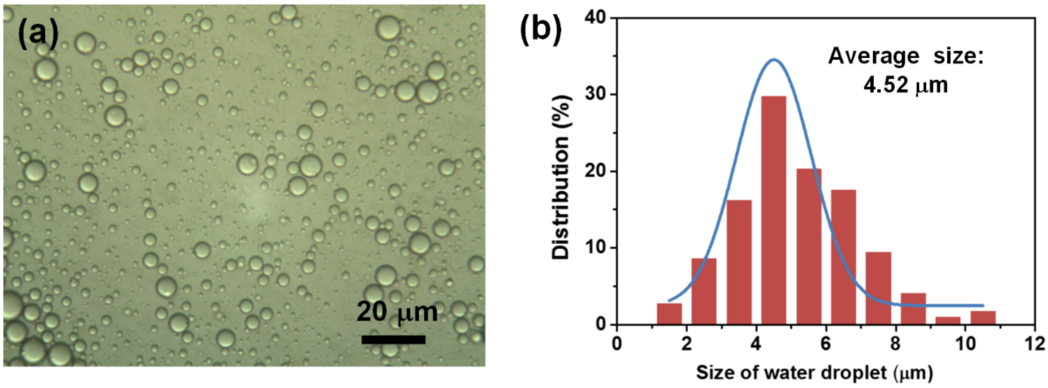

Fig. S5 (a) Optical microscopic image of and as-prepared oil/water emulsions. (b) Histogram showing the oil droplet size distribution in emulsions.