In-situ synthesis of flexible magnetic γ-Fe_2O_3@SiO_2 nanofibrous membranes

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Support information

Materials

Poly(vinyl alcohol) (PVA, M_w=88000), phosphoric acid (H_3PO_4, 85%), bisphenol-A, paraformaldehyde, aniline, ferric acetylacetonate ($Fe(acac)_3$), sodium hydroxide (NaOH), tricholoromethane, acetone, sodium hydroxide, and anhydrous magnesium sulfate 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 SNF membranes

The precursor solution was prepared by dissolving the PVA in pure water at 80°C with vigorous stirring for 12 h. The silica gel was generated from the hydrolysis and polycondensation of TEOS, by dropwise addition of H_3PO_4 and H_2O to TEOS with the molar composition of TEOS:H_2O:H_3PO_4:=1:11:0.01. Following, 20 g resultant silica gel was added into the PVA (20 g) solution and stirred for another 5 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 17 kV and a controllable feed rate of 1 mL/h. Finally, the composite membranes were calcined to 800°C by gradually increasing the temperature at the heating rate of 5 °C/min in air to remove the PVA.

Synthesis of BA-a monomer

The BA-a was synthesized by using bisphenol-A, aniline, and paraformaldehyde via a one-step Mannich reaction (Fig. S1). Briefly, 20 g of bisphenol-A, 10.52 g of paraformaldehyde and 16.32 g of aniline were added into a three necked flask with stirring for 20 min. Then the temperature was gradually increased to 100°C and kept at 100°C-110°C for 4 h. After cooling to room temperature, the obtained product was dissolved in 200 mL of tricholoromethane. The solution was purified by washing with 1 wt% sodium hydroxide and pure water, then treated with anhydrous magnesium sulfate and filtered, and dried at 60°C for 2 h to obtain BA-a monomers. The detail of structural confirmation by ^{1}H NMR spectroscopy were presented in Fig. S2.

Fabrication of γ-Fe_2O_3@SNF membranes

The as-prepared SNF membranes were firstly dipped in the acetone solutions with 2% of BA-a and 8% of $Fe(acac)_3$ for 5 min. Following the membranes were dried in the oven for 20 min at 60°C, and then in situ polymerization of BA-a was carried out at 200°C in vacuum for 1 h, leading to the formation of the Mannich bridge cross-linked structure, and generating cured thermosetting PBZ layer on fiber surface which contained embedded $Fe(acac)_3$ (PBZ/SNF). The thickness of this PBZ layer will increase with the increasing of BA-a concentration and the dipping time. Finally, the PBZ/SNF membranes were calcined at 850 °C for 30 min with the heating rate of 2 °C/min under N_2 flow (the N_2 flow rate was 0.002 m^3/min), and yielded the magnetic γ-Fe_2O_3@SNF membranes.

Magnetic adsorption measurement

The adsorption performance of γ-Fe_2O_3@SNF membranes were tested by the removing of two typical dye pollutants of methylene blue (MB). Generally, 20 mg of γ-Fe_2O_3@SNF was immersed into the test aqueous solution (MB, 1×10^{-5} M, 20 ml) with slight 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, as shown in Fig. S7.

Characterization

The ^{1}H NMR spectrum was recorded using the Bruker Avance 400, d_6-DMSO was used as the solvent. FT-IR spectra were performed with a Nicolet 8700 FT-IR spectrometer in the range 4000-400 cm^{-1}. Field emission scanning electron microscopy (FE-SEM) images and energy-dispersive X-ray (EDX) spectroscopy images were examined by Hitachi S-4800, Hitachi Ltd., Japan. Transmission electron microscopy images were measured by using JEM-2100F, JEOL Ltd., Japan. N_2 adsorption-desorption isotherms were examined at 77 K by an ASAP 2020 physisorption analyzer (Micromeritics Co., USA). The phase structure was characterized with X-ray diffraction (XRD) (D/Max-2550 PC Rigaku Co., Japan). Magnetic properties were measured with a vibrating sample magnetometer (VSM, Lake Shore 7304, USA).

The determination of the crystallite size of the γ-Fe_2O_3

The average crystallite size of the γ-Fe_2O_3 nanoparticles were calculated by the Scherrer's formula: $D=0.89\lambda/\beta\cos\theta$. where D is the average crystallite size of γ-Fe_2O_3, λ is the X-ray wavelength, β denotes the full width at half maximum (FWHM) intensity, and θ means the Bragg angle.

Supplementary Discussing

The formation of γ-Fe_2O_3 nanoparticles during calcination could be explained by the burst-nucleation and crystal growth mechanism. Generally, this conversion comprises three correlative procedures. Firstly, the pyrolysis of $Fe(acac)_3$ generated numerous of iron compound monomers due to a series of complicated decomposition reactions and redox reactions. Subsequently, as the monomer concentration exceeded the critical concentration, the monomers fiercely aggregate to form nuclei (clusters). Finally, after the burst-nucleation process, the monomer concentration decreased, and the nuclei gradually growth into γ-Fe_2O_3 nanocrystal by the consumption of monomers.[1-5] Moreover, the second nuclei formation procedure and the final burst-nucleation procedure greatly rely on the stability of matrix environmental for grain growth. The PBZ layers provide good dimensional stability and carbon cladding for γ-Fe_2O_3 nucleis, which improves the growth of γ-Fe_2O_3 grains. [6-8]

References

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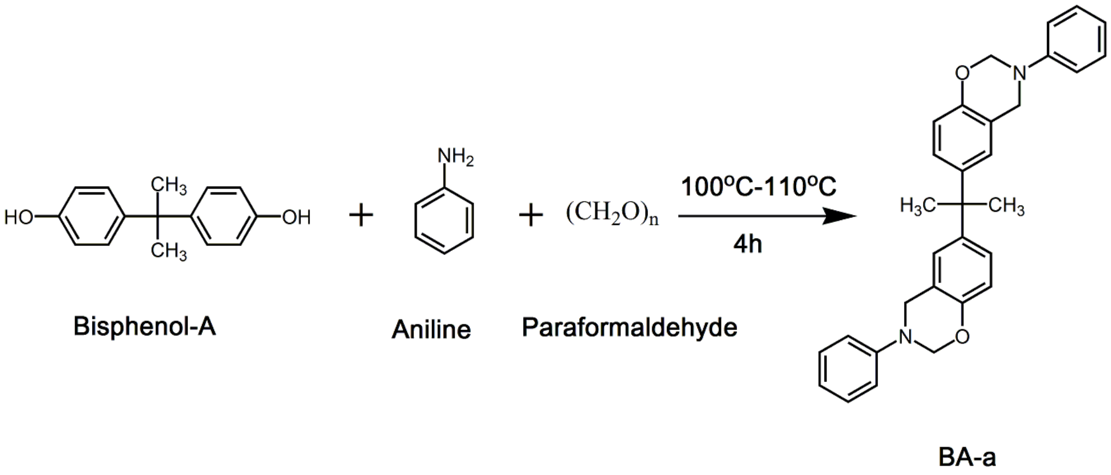

Fig. S1 Schematic representation of the synthesis of BA-a via Mannich reaction.

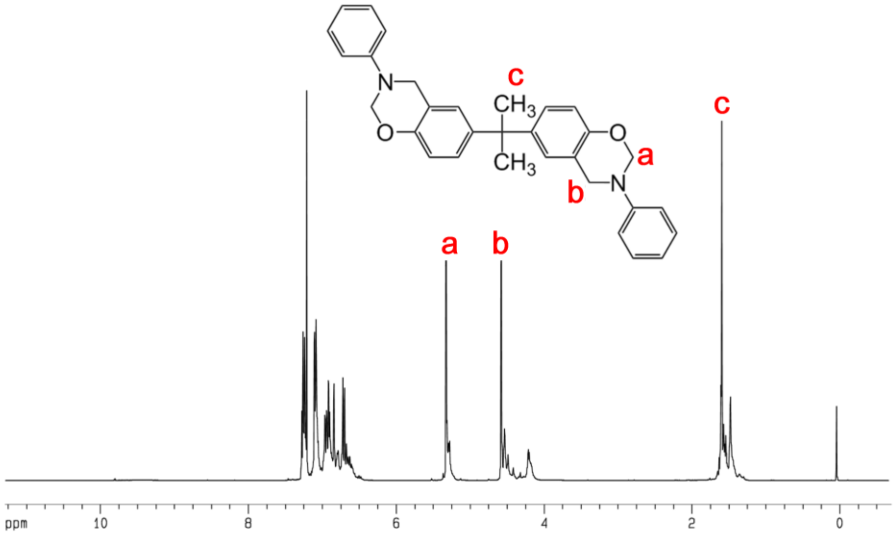

Fig. S2 ^{1}H NMR spectrum of as-synthesized BA-a, *d*-$CHCl_3$ was used as the solvent.

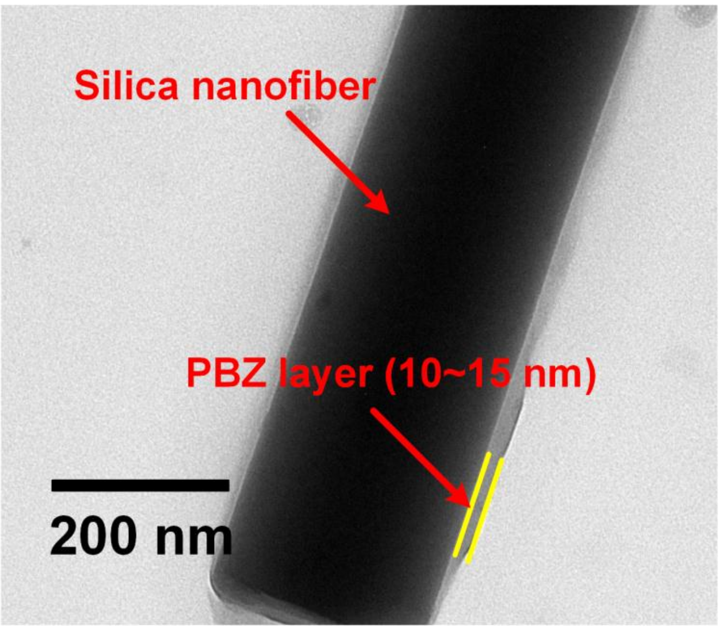

Fig. S3 TEM image of the PBZ/SNF membranes shows the well coated PBZ layer with the uniform thickness of 10~15 nm.

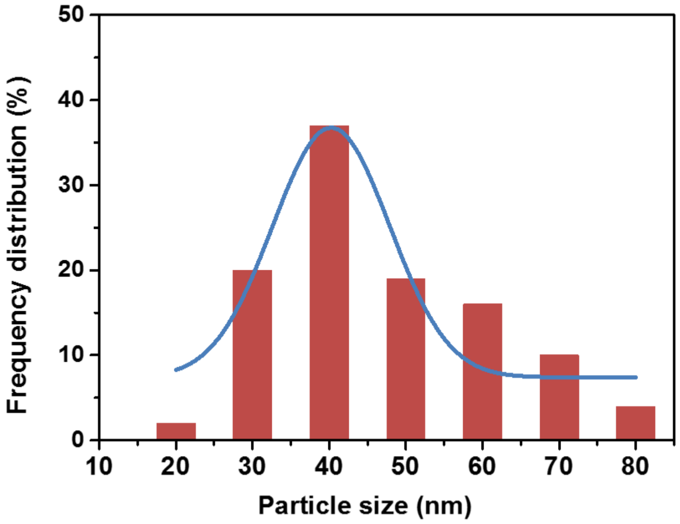

Fig. S4 Histogram showing the size distribution of γ-Fe_2O_3 nanoparticles.

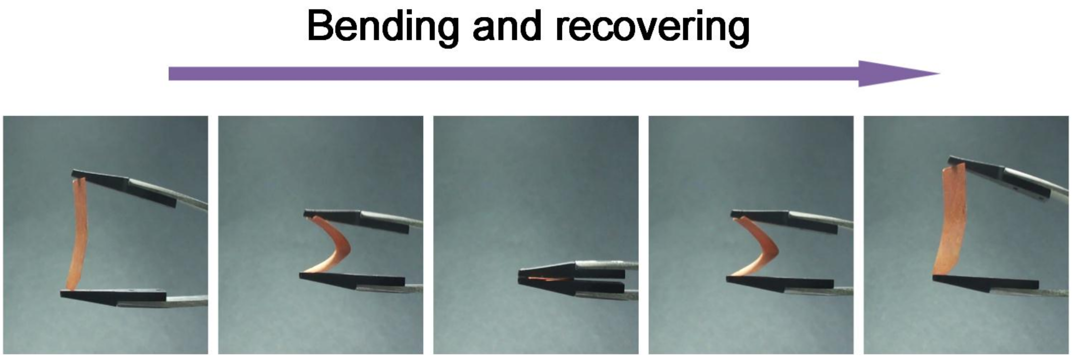

Fig. S5 Optical images presenting the promising flexibility of γ-Fe_2O_3@SNF membranes by facilely bending and recovering.

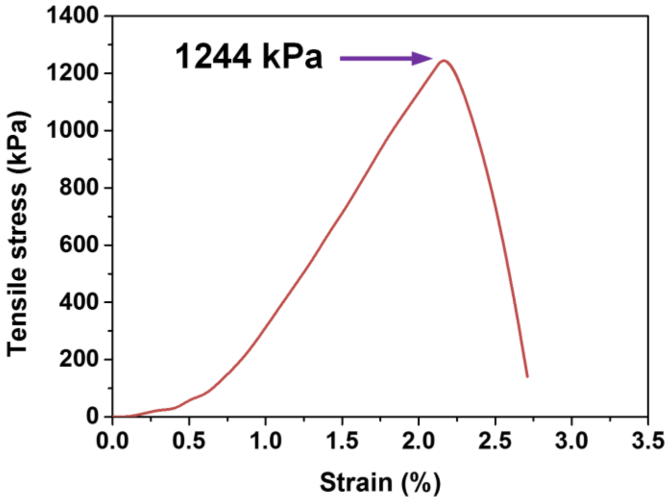

Fig. S6 Stress-strain curve of γ-Fe_2O_3@SNF shows the robust strength of 1244 kPa.

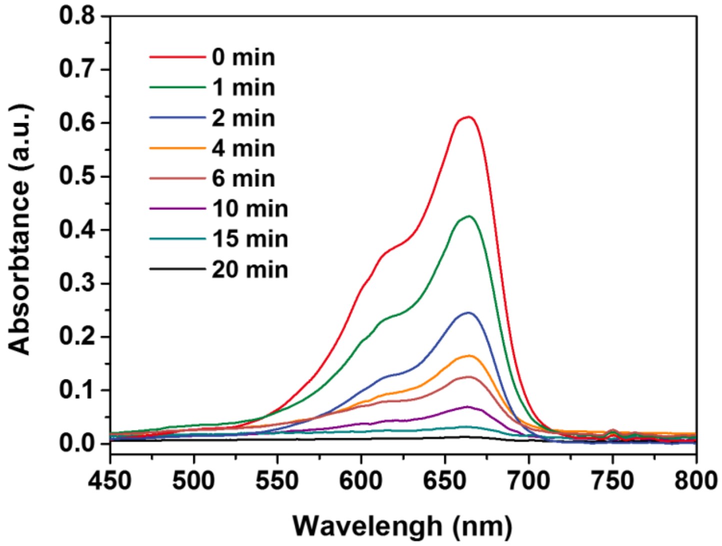

Fig. S7 UV-Vis spectra of MB solution (1×10^{-5} M) and after treatment with γ-Fe_2O_3@SNF for various time.