

Electronic Supplementary Information (ESI)

Synthesis of mesoporous magnetic Fe₃O₄@Carbon nanofibers utilizing in-situ polymerized polybenzoxazine for water purification

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Experimental Section

Materials

PVB ($M_w=170000-250000$), bisphenol-A, ferric acetylacetonate (Fe(acac)₃), paraformaldehyde, aniline, sodium hydroxide (NaOH), hydrochloric acid, anhydrous magnesium sulfate, dimethylformamide (DMF), tetrahydrofuran (THF), chloroform were purchased from Shanghai Chemical Reagents Co., Ltd., China. MilliQ water with a resistance of 18.2 MΩ was obtained from a Heal Force NW ultrapure water system (Heal Force, Co., Ltd., China). All chemicals were of analytical grade and were used as received without further purification.

Synthesis of 2,2-bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)propan (BA-a) monomer

The BA-a was synthesized by using bisphenol-A, paraformaldehyde and aniline via a one step Mannich reaction (Fig. S1). Typically, 30 g of bisphenol-A, 15.78 g of paraformaldehyde and

24.48 g of aniline were added into a three necked flask with stirring at room temperature for 30 min. Then the temperature was gradually increased to 105°C and the reaction proceeded at 100°C-105°C for 4 h. After cooling to room temperature, the obtained product was dissolved in 150 ml chloroform. In order to remove the remnant of raw materials, the solution was washed with NaOH (2 wt%) aqueous solution and MilliQ water, then treated with anhydrous magnesium sulfate, and dried through rotary evaporation at 50°C for 2 h to obtain BA-a powder. The ¹H nuclear magnetic resonance (NMR) spectra of the BA-a is shown in Fig. S2.

Fabrication of the PVB/BA-a/Fe(acac)₃ (PVBNF) composite nanofibers

A typically procedure for fabrication of the PVBNF membranes is as follows. The precursor solution was prepared by dissolving 1.5 g of BA-a and 0.3 g Fe(acac)₃ of in 7.7 g of DMF/THF mixed solution (the weight ratio is 1:1), after stirring for 1 h, 0.5 g of PVB was added slowly into the solution and the mixture were stirred for another 4 h. The resulting viscous solution was transferred into a syringe and injected through a metal needle that was connected to a high-voltage supply (DW-P303-1ACD8, Tianjin Dongwen High Voltage Co., China). The solution was fed at a constant and controllable rate of 1 mL/h by using a syringe pump (LSP02-1B, Baoding Longer Precision Pump Co., Ltd., China). A high voltage of 20 kV was applied to the needle tip, resulting in the generation of a continuous jetting stream. The composite nanofibers were collected on the surface of a grounded aluminum foil (tip to collector distance was 15 cm) and dried at room temperature under vacuum for 1 h.

Preparing of Fe₃O₄@CNFs

In a typical experiment, the PVBNF membranes were put into a vacuum oven with an external tension, and then the in situ polymerization was carried out at 230°C under vacuum for 30 min to get thermosetting PBZ nanofibers (PBZNF). Subsequently, the obtained PBZNF was immersed into the KOH aqueous solution (30 wt%) with slightly stirring for 1h, following dried at 60°C under vacuum. Finally, 2 g of activated PBZNF (A-PBZNF) membranes were put into a furnace, and then the temperature was gradually increased to 850°C for 30 min with the heating rate of 2°C/min under N₂ flow (the N₂ flow rate was 0.002 m³/min). After carbonization, the products were washed with 0.1 M HCl, and the black activated Fe₃O₄@CNFs (A-Fe@CNF) was obtained.

In addition, the unactivated Fe₃O₄@CNFs (Fe@CNF) was also prepared for comparison.

Techniques of characterization

The morphology of nanofibers was examined by using a field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi Ltd., Japan) and transmission electron microscopy (TEM) (JEM-2100F, JEOL Ltd., Japan). Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet 8700 FT-IR spectrometer in the range 4000-400 cm⁻¹. Raman spectra were examined by using a micro-Raman spectroscopy system (inVia-Reflex, Renishaw, Co., UK). ¹H NMR spectrum was recorded on a Bruker Avance 400 (resonance frequency of 400 MHz for ¹H), *d*₆-CHCl₃ was used as the solvent. The Brunauer-Emmet-Teller (BET) surface area was characterized by using N₂ adsorption-desorption isotherms with a surface area analyzer (ASAP 2020, micromeritics Co., USA). The phase structure was characterized with X-ray diffraction (XRD) (D/Max-2550 PC Rigaku Co., Japan). Synchrotron radiation small-angle X-ray scattering (SAXS) measurements were performed at Beamline XB16L of Shanghai Synchrotron Radiation Facility. Magnetic properties were measured with a vibrating sample magnetometer (VSM, Lake Shore 7304, USA). The UV-Vis absorption spectra were measured by using an Ideaoptics FX4000+ spectrometer (Ideaoptics Technology Ltd., China).

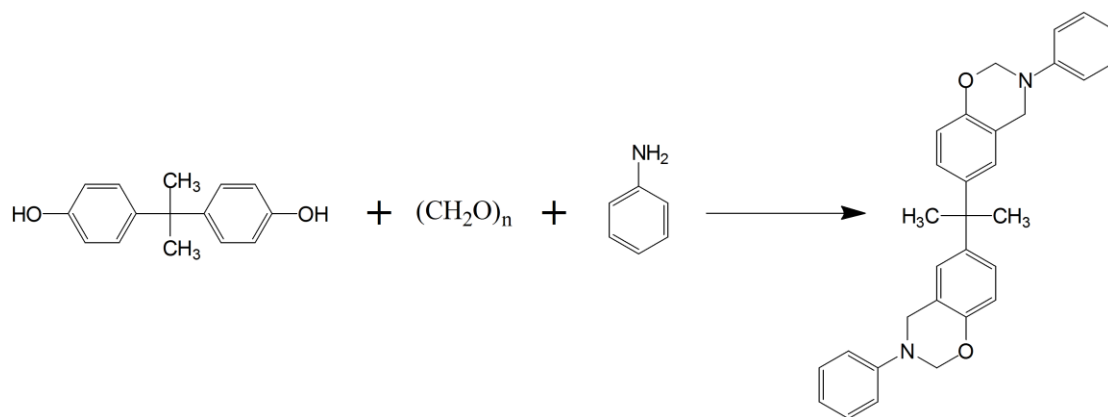


Fig. S1 Schematic representation of the synthesis of BA-a via Mannich reaction.

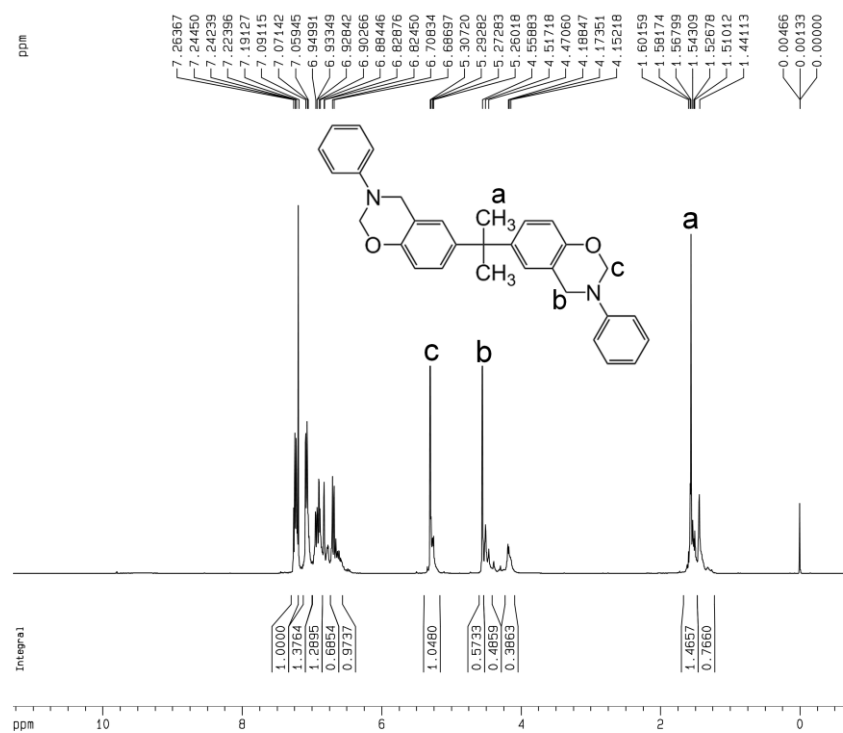


Fig. S2 ¹H NMR spectrum of as-synthesized BA-a, *d*₆-CHCl₃ was used as the solvent.

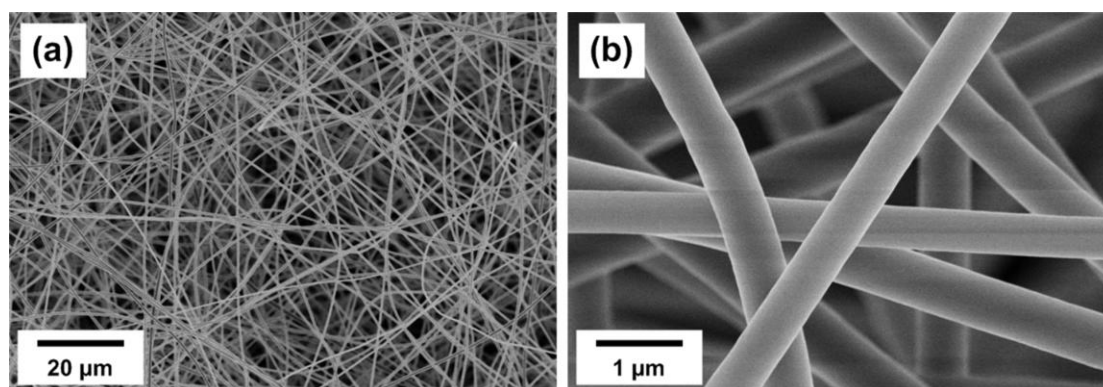


Fig. S3 (a, b) FE-SEM images of the as-prepared PVBNF membranes.

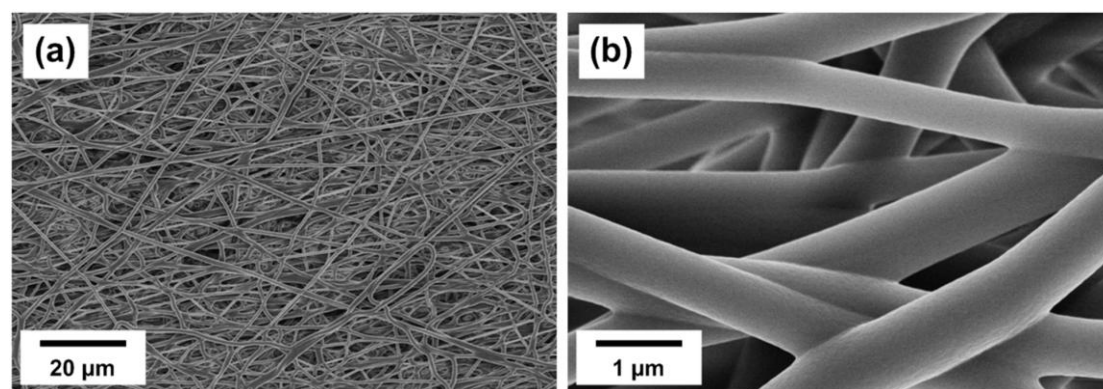


Fig. S4 (a, b) FE-SEM images of the as-prepared PBZNF membranes.

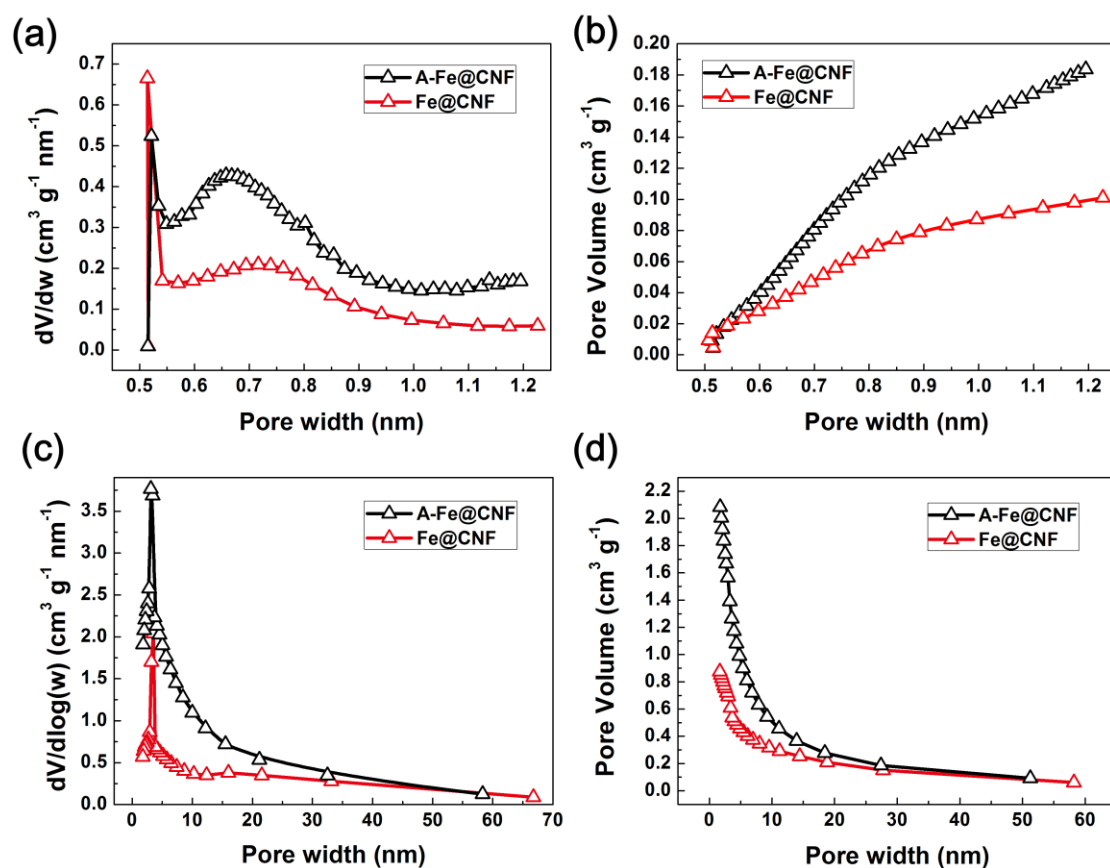


Fig. S5 (a, b) Horvath-Kawazoe (HK) microporous analysis and (c, d) Barrett-Joyner-Halenda (BJH) mesoporous analysis of A-Fe@CNF and Fe@CNF samples.

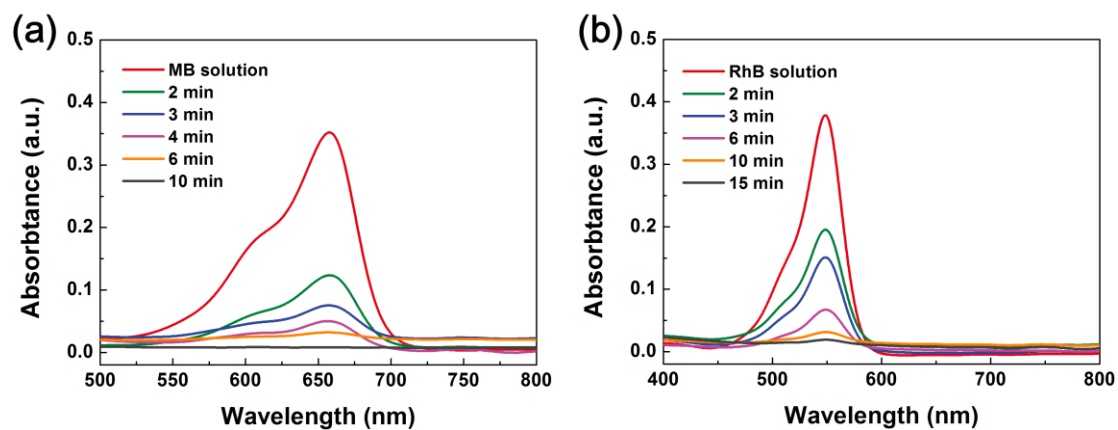


Fig. S6 UV-Vis spectra of (a) MB solution (1 × 10⁻⁵ M) and (b) RhB solution (1 × 10⁻⁵ M) after treatment with A-Fe@CNF for various time.