Electronic Supplementary Material (ESI) for Nanoscale

Synthesis of superhydrophobic silica nanofibrous membranes with robust thermal stability and flexibility via in situ polymerization

Liping Yang,‡*[a,b]* **Aikifa Raza,**‡*[a]* **Yang Si,***[a]* **Xue Mao,***[a]* **Yanwei Shang,***[a,b]* **Bin Ding*****[a,c,d]* **and Jianyong Yu***[d]*

[a] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China. E-mail: binding@dhu.edu.cn

[b] College of Textiles, Donghua University, Shanghai 201620, China

[c] College of Materials Science and Engineering, Wuhan Textile University, Wuhan 430073, China

[d] Nanomaterials Research Center, Modern Textile Institute, Donghua University, Shanghai 200051, China

‡ These authors have contributed equally to this work.

Chemical Synthesis of 2,2-bis(3-*m*-(Trifluoromethyl)anilinel-3,4-dihydro-2H-1,3-benzoxazinyl)hexafluoro propane (BAF-tfa)

The BAF-tfa monomer was synthesized using 4,4'-(Hexafluoroisopropylidene) disphenol (BAF, 98%), *m*-(trifluoromethyl)aniline (tfa), and paraformaldehyde through Mannich reaction (Fig. S1). Typically, 44.18 g of BAF, 15.78 g of paraformaldehyde and 42.35 g of tfa were added into a three necked round bottom flask. The raw chemicals were stirred at room temperature for 30 min. Then the temperature was gradually increased to 110°C with continued stirring for 4 h in an inert atmosphere. After cooling to room temperature, the obtained yellow colour product was dissolved in 100 mL of tricholoromethane. The monomer (BAF-tfa) solution was purified by washing three times with 2 wt% aqueous sodium hydroxide and three times with Milli-Q water. The solution was treated with anhydrous calcium chloride and then filtered, and dried through rotary evaporation at 60°C for 4 h to obtain BAF-tfa powder.

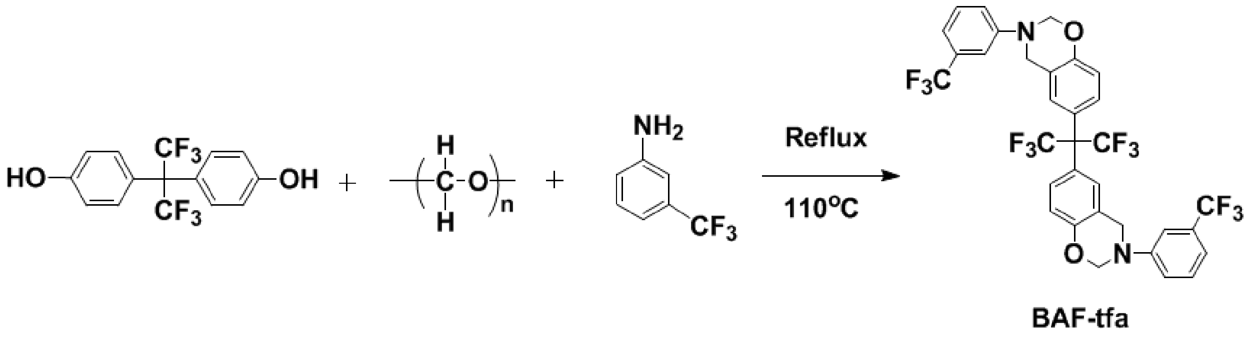

Fig. S1 Illustration showing the synthesis of BAF-tfa via Mannich reaction.

Structural confirmation of BAF-tfa

The as-synthesized BAF-tfa monomer after purification and crystallization was subjected to nuclear magnetic resonance (NMR) spectroscopic analysis. Fig. S2 illustrates the ^{1}H NMR spectrum of BAF-tfa. For pure BAF, the peak for Ar–OH appeared at 9.16 ppm, while signals for aromatic protons appeared at 6.98 and 6.64 ppm. In case of pure tfa, the proton for amine group has given chemical shift at 3.7 ppm while aromatic protons have given signals around 6.8-7.2 ppm (Fig. S2 above). Specific for oxazine ring, the peaks for Ar–CH_2–N and N–CH_2–O are observed in ^{1}H NMR, which are distinctive of benzoxazine monomers.[1-3] For BAF-tfa monomer, the characteristic protons of Ar–CH_2–N and N–CH_2–O appeared at 4.63 ppm, and 5.46 ppm. Moreover, aromatic protons have given their chemical shift in the range of 6.81-7.46 ppm (Fig. S2 below). ^{19}F NMR has given further structural affirmation of BAF-tfa monomer (Fig. S3). The chemical shift for N–Ar–CF_3 is appeared at 120.26 ppm, while for C–CF_3 at 63.92ppm.[4] Acquisition of quantitative results from all NMR analysis has confirmed the chemical structure of BAF-tfa.

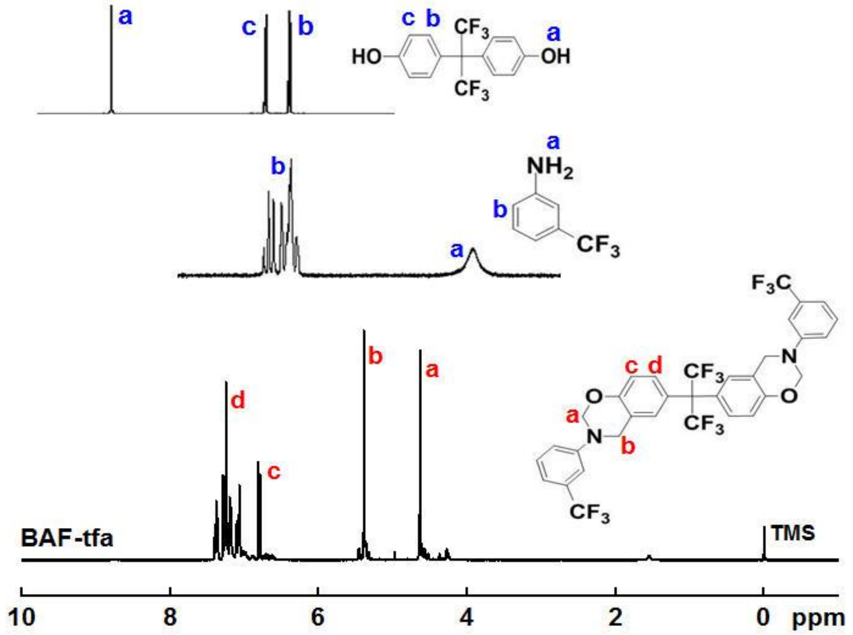

Fig. S2 ^{1}H NMR spectrograph of fluorinatedbisphenol A, *m*-(trifluoromethyl)aniline (above), and the reaction product of BAF, tfa, and paraformaldehyde (BAF-tfa) (below).

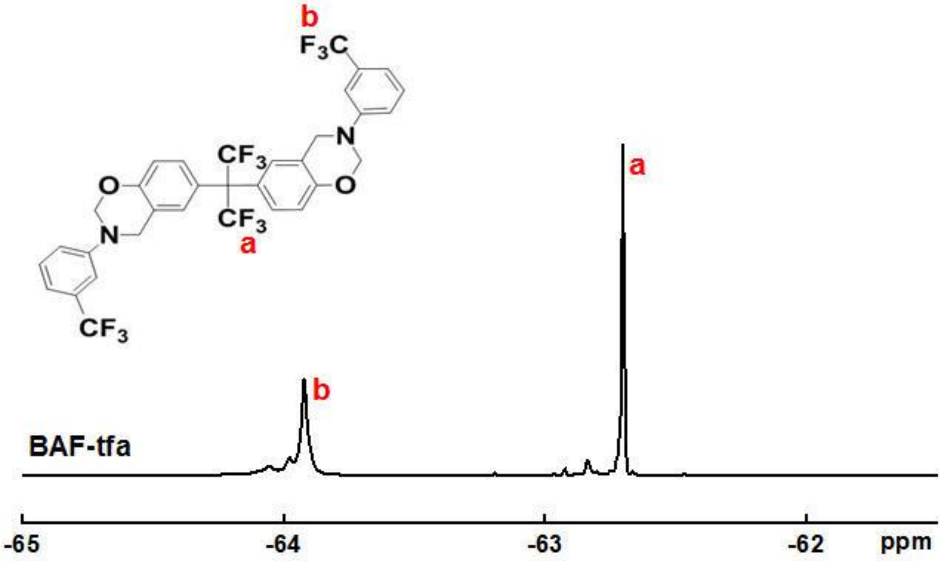

Fig. S3 ^{19}F NMR spectrograph of BAF-tfamonmer.

Functional group affirmation of pure and modified silica membranes

To check the role of chemical wettability imparted by F-PBZ to the silica nanofibrous membranes, an IR spectroscopic analysis was performed. Fig. S4 shows the comparative FT-IR spectra of pure PVA, hybrid PVA/silica, pure silica, and F-PBZ/SiO_2 NPs modified silica membranes before and after curing. The absorption features of PVA were found at 3357 cm^{-1} (-OH), 2939 cm^{-1} ($-CH_2$), 1740 cm^{-1} (C=O), 1450 cm^{-1} (O=C-OR), 1340 cm^{-1} ($-CH_2$), and 1110 cm^{-1} (C-O-C), respectively (Fig. S4a).[5] Fig. S4b shows the FT-IR spectra of PVA/silica nanofibrous membranes, and besides some absorption features of PVA, the absorption peaks at 1100, 790, and 470 cm^{-1} were also observed in the case of the Si-O-Si bond along with the peak around 929 cm^{-1} for Si-OH bond.[6, 7] After calcination the absorption band for PVA completely disappeared, (Fig. S4c) confirming the complete removal of organic part of the membranes. After F-PBZ/SiO_2 modification, the nanofibers were again subjected to FT-IR analysis for the confirmation of cross-linking of BAF-tfa on the surface of nanofibers. The characteristic bands (for monosubstituted benzene) at 720 and 692 cm^{-1} did not appear,[8, 9] however, the typical distinguishing bands for oxazine ring at 830 cm^{-1} and for C–O–C at 945 cm^{-1}appeared with the adsorption band for trisubstituted benzene ring at 1320 cm^{-1} (Fig. S4d). The decrease in peak resolution of this band for trisubstituted benzene ring have pointed out the ring-opening phenomenon in oxazine and thus validating the transformation of monomers into oligomers and polymers within the silica nanofibrous membranes (Fig. S4e).

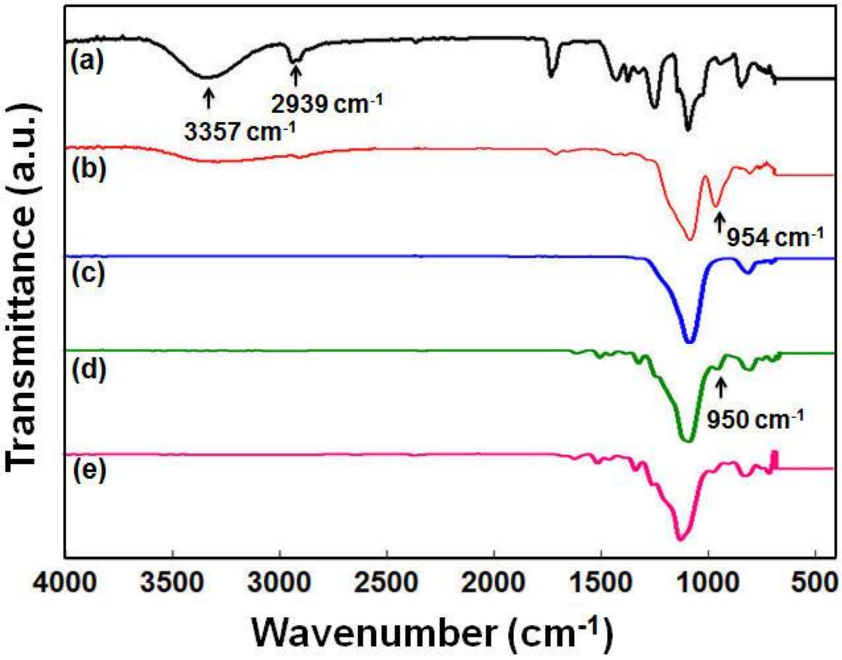

Fig. S4 FT-IR spectra of various fibrous membranes of (a) pure PVA. (b) PVA/silica. (c) SNF. (d) F-PBZ/SiO_2 NPs modified silica membranes before curing. (e) F-PBZ/SiO_2 NPs modified silica membranes after curing.

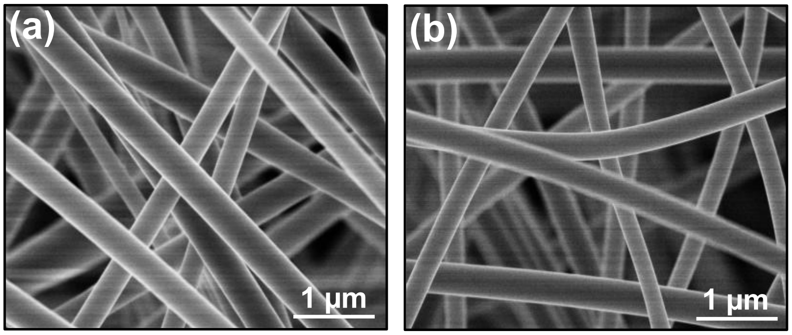

Fig. S5 FE-SEM images of (a) PVA/silica precursor nanofibrous membranes and (b) silica nanofibrous membranes.

References

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