Supplementary Material:

Porous Membrane Controlled Polymerization of Nanofibers of Polyaniline and Its Derivatives

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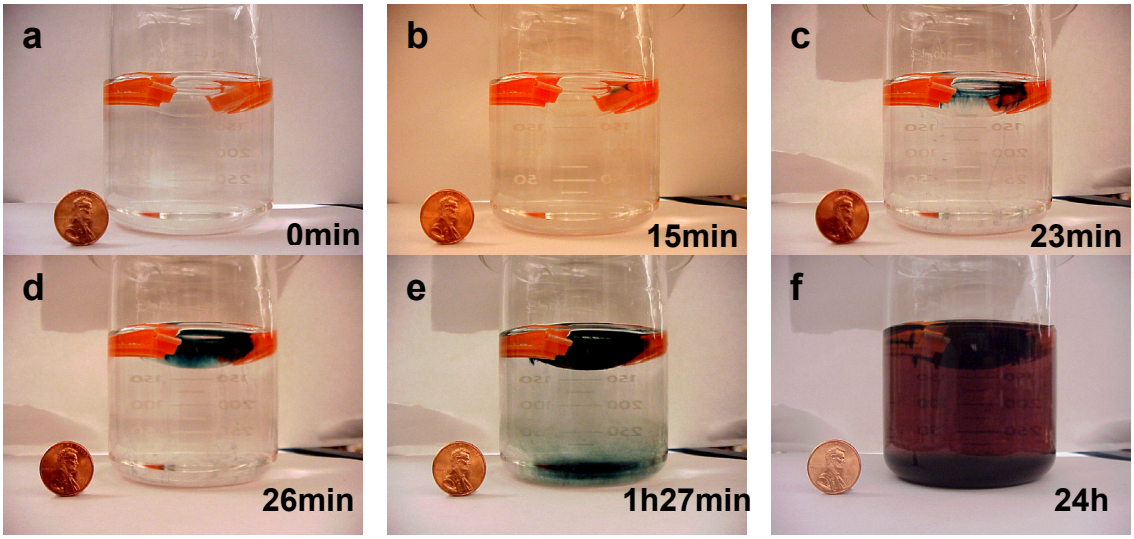
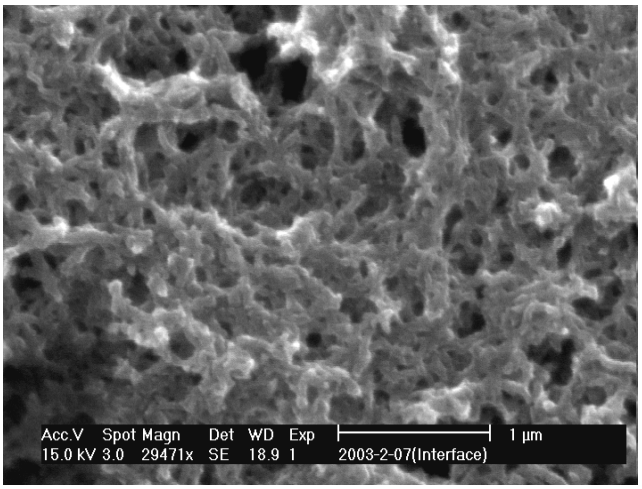
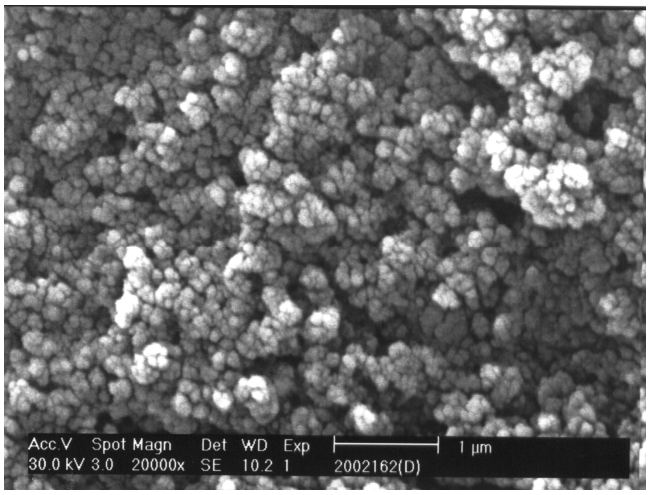


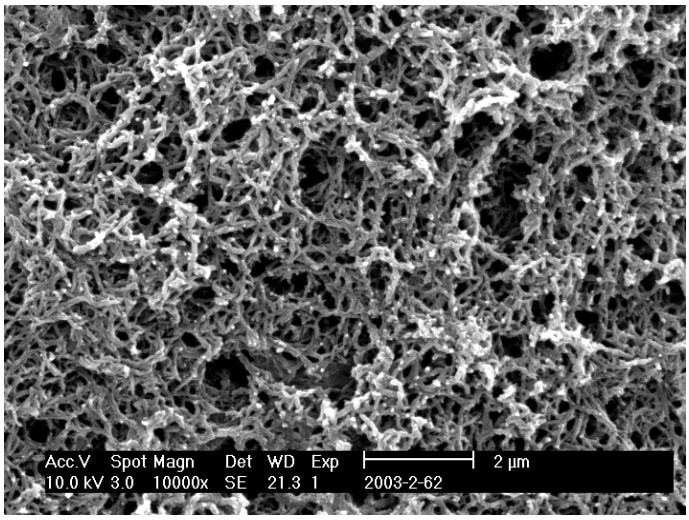
Supporting Figure 1. Photographs illustrating PMCP using as an example Spectra/Por® Dialysis Tubing (MWCO: 12k-14k; flat width: 25mm), [HCl]=1.2M, [aniline]=1.61mmoles / 5ml of 1.2M HCl (inside the tubing), and [APS]=0.8mmoles / 200ml of 1.2M HCl (outside the tubing). The images were captured after the filled porous membrane (dialysis tubing) was introduced into the beaker at elapsed times of a) 0min, b) 15min, c) 23min, d) 26min, e) 1h 27min and f) 24h. A blue green color was observed near the membrane when the polymerization started. As time proceeded, the green (characteristic of emeraldine salt) nanofibers tended to precipitate due to their agglomeration. After 24 hours, the color of the polymerization solution became deep pink, suggesting presence of some residual oligomers. The orange color bars on images are Spectra/Por® Closures used to seal the tubing. A supplementary video of the polymerization is also provided.



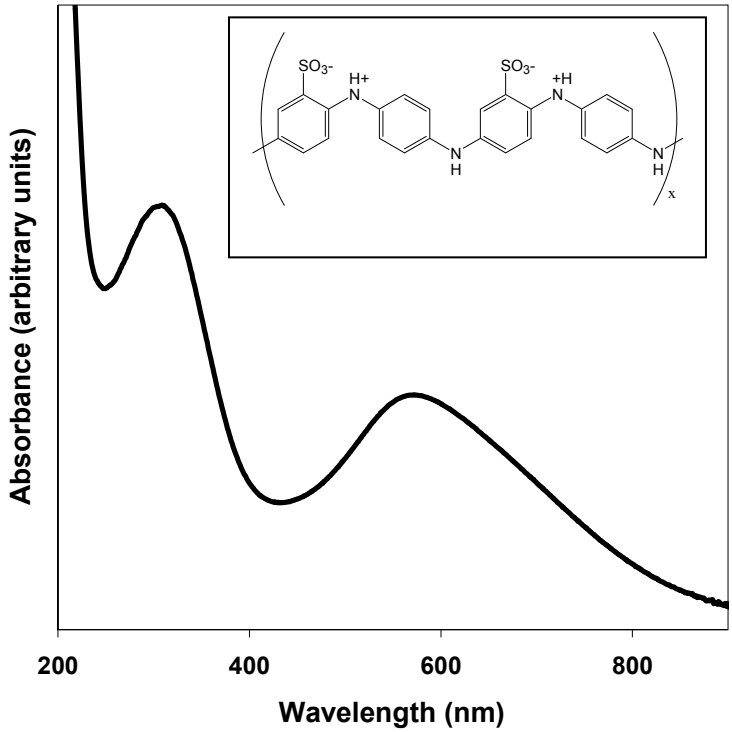
Supporting Figure 2. Scanning electron micrograph (SEM) of sulfonated polyaniline nanofibers prepared by interfacial polymerization. Polymerization conditions: [aniline] = 1.61mmoles/40ml toluene (organic phase), and [metanilic acid] = 3.22mmoles and [APS] = 0.8mmoles/40ml of 1.0M HCl (aqueous phase), temperature = ~24 °C, reaction time = 24h and without disturbance. This contrasts with the fibrous morphology of sulfonated polyaniline obtained via PMCP (Fig. 2(b)).



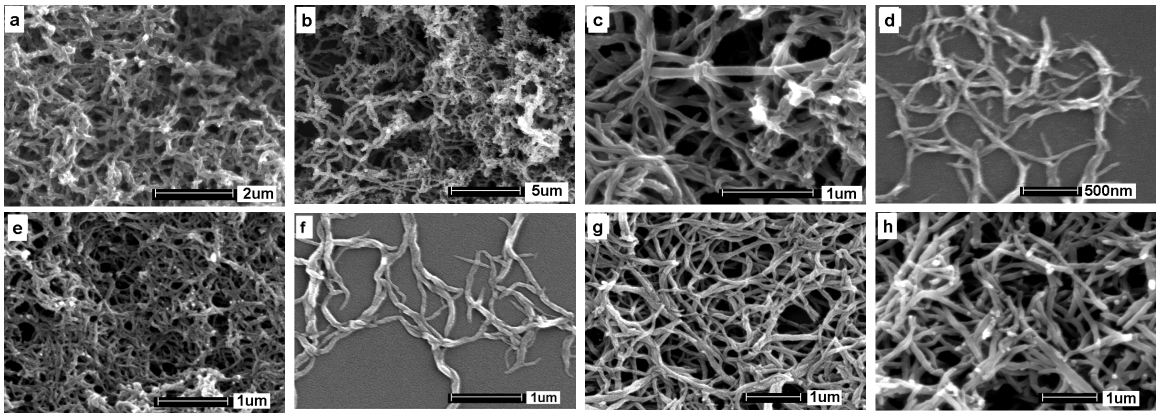
Supporting Figure 3. Scanning electron micrograph (SEM) of poly (*o*-toluidine) prepared by interfacial polymerization. Polymerization conditions: [*o*-toluidine] = 1.87mmoles/40ml toluene (organic phase), and [APS] = 1.87mmoles/40ml of 1.0M HCSA (aqueous phase), temperature = ~24°C, reaction time = 26h and without disturbance. This contrasts with the fibrous morphology of poly (*o*-toluidine) obtained via PMCP (Fig. 2(c)).



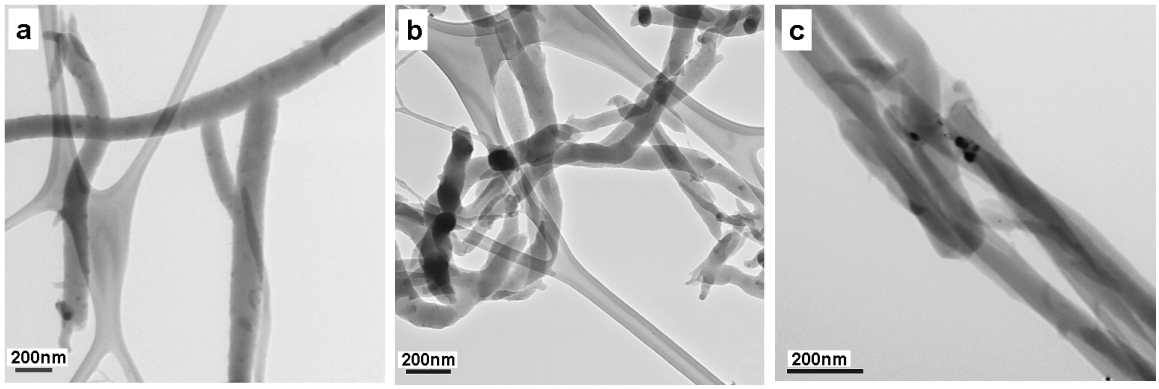
Supporting Figure 4. Scanning electron micrograph (SEM) of polyaniline-CH_3SO_3H nanofibers synthesized by PMCP at room temperature using dialysis tubing with MWCO of 3,500. Pure aniline (without adding any solvent or acid solution) was loaded inside dialysis tubing. The precipitate was collected outside dialysis tubing.



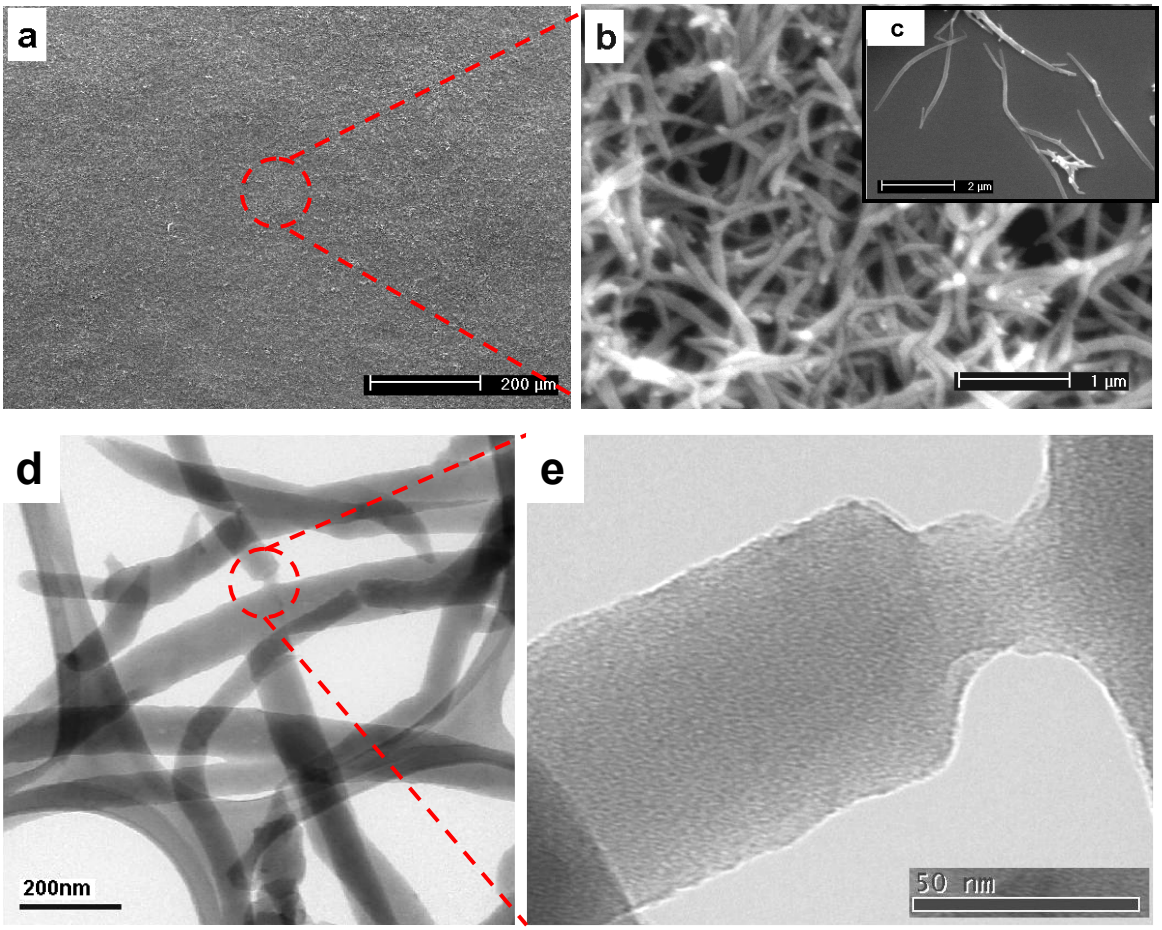
Supporting Figure 5. UV-vis spectrum of copolymer nanofibers of sulfonated polyaniline synthesized by PMCP using the polymerization condition as described in Figure S7. Inset: schematic chemical structure of sulfonated polyaniline for 50% sulfonation.



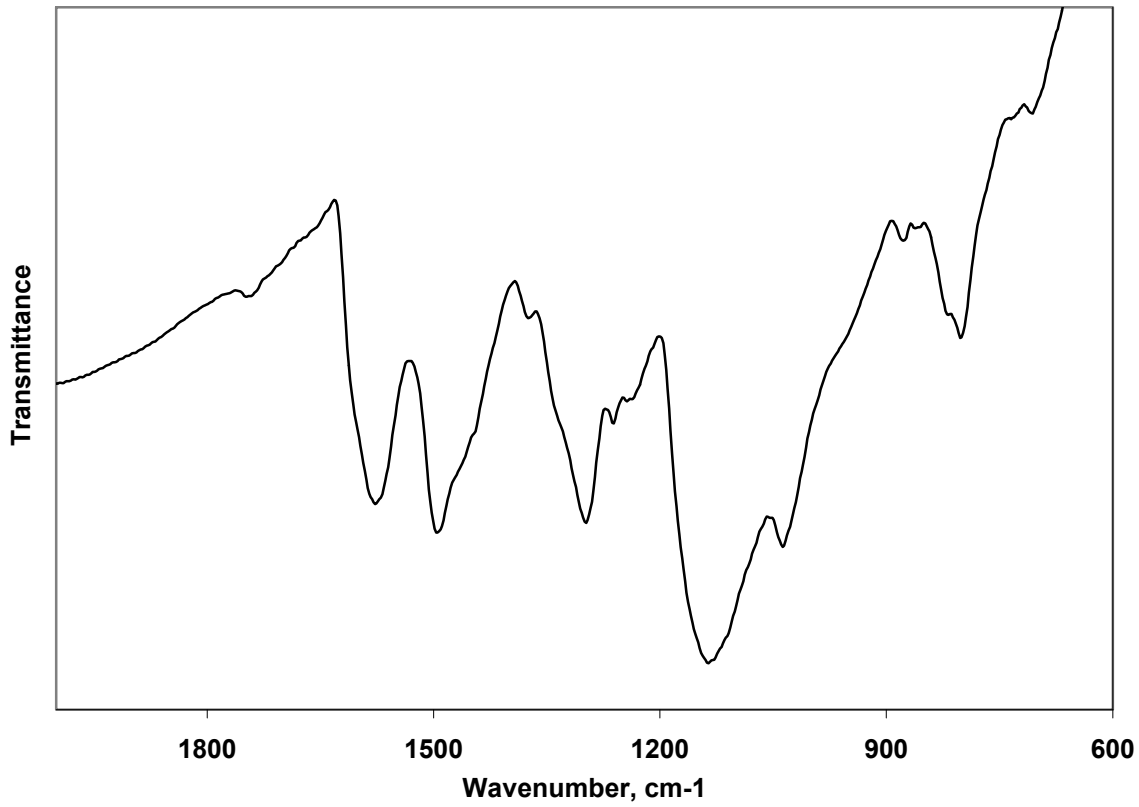
Supporting Figure 6. Scanning electron micrograph (SEM) of polyaniline nanofibers deposited on Si-wafer substrate with a thin layer coating of Au/Pd. Polymerization conditions: a)-e) Spectra/Por Dialysis Tubing (MWCO: 12k-14k; Flat width: 25mm) [aniline]=1.6mmoles/5ml of 1.0M dopant acid (inside the tubing), and [APS]=0.8mmoles/200ml of 1.0M dopant acid (outside the tubing) at room temperature. f)-h) Spectra/Por3.1 Dialysis Tubing (MWCO: 3,500; Flat width: 18mm) [aniline]=1.6mmoles/3ml of 1.0M dopant acid (inside the tubing), and [APS]=0.8mmoles/200ml of 1.0M dopant acid (outside the tubing) at room temperature. A variety of dopant acids were used, such as (a) HCl (b) H_2SO_4 (c) AMPSA (d) H_3PO_4 (e) *p*-TSA (f) HCSA (g) CH_3SO_3H and (h) $HClO_4$. Aniline to APS molar ratio was kept at 2.



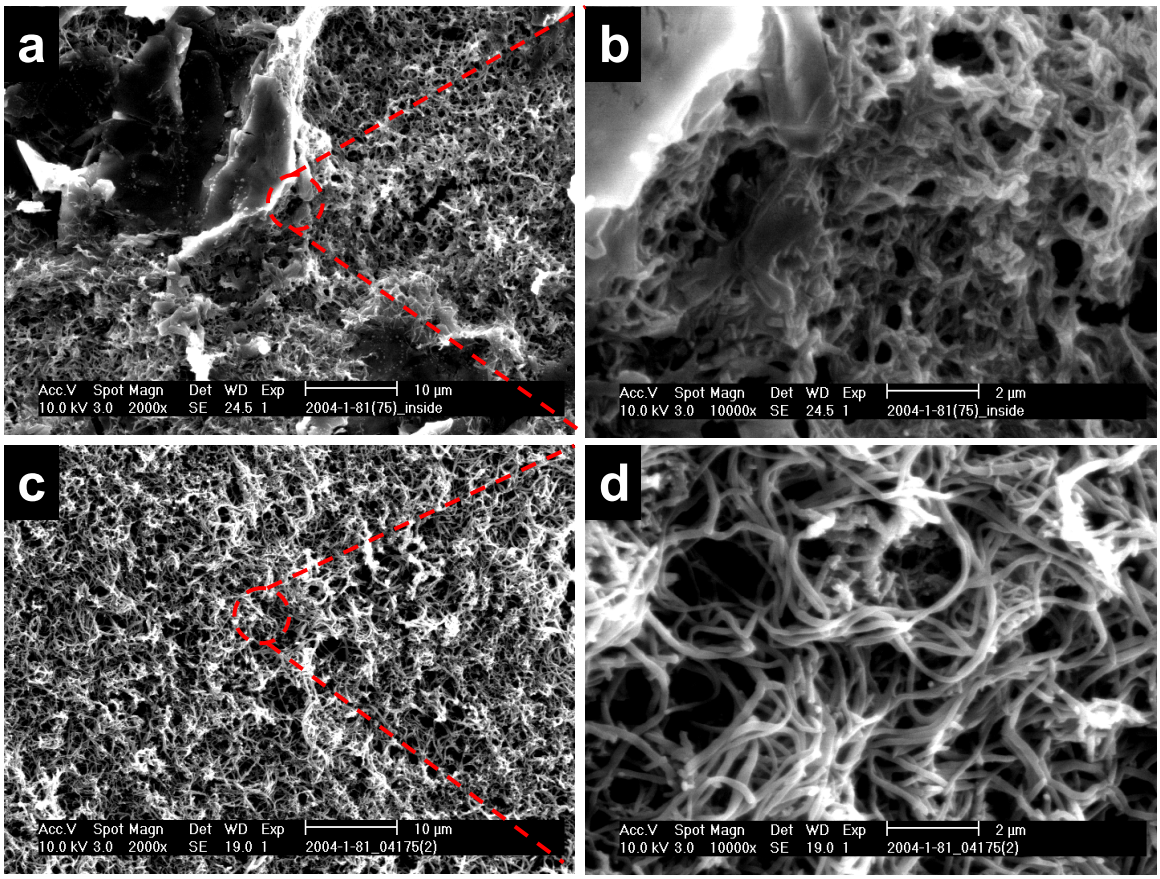
Supporting Figure 7. Transmission electron micrograph (TEM) of polyaniline-$HClO_4$ nanofibers dispersed in ethanol under ultrasonic bath, and then deposited on copper grid substrate. Polymerization conditions: Spectra/Por3 Dialysis Tubing (MWCO: 3,500; Flat width: 45mm), [$HClO_4$]=1.0M, [aniline]=4.025mmoles/12ml of 1.0M $HClO_4$ (inside the tubing), and [APS]=4.025mmoles/500ml of 1.0M $HClO_4$ (outside the tubing) at room temperature. a)-c) TEM images are taken in different area.



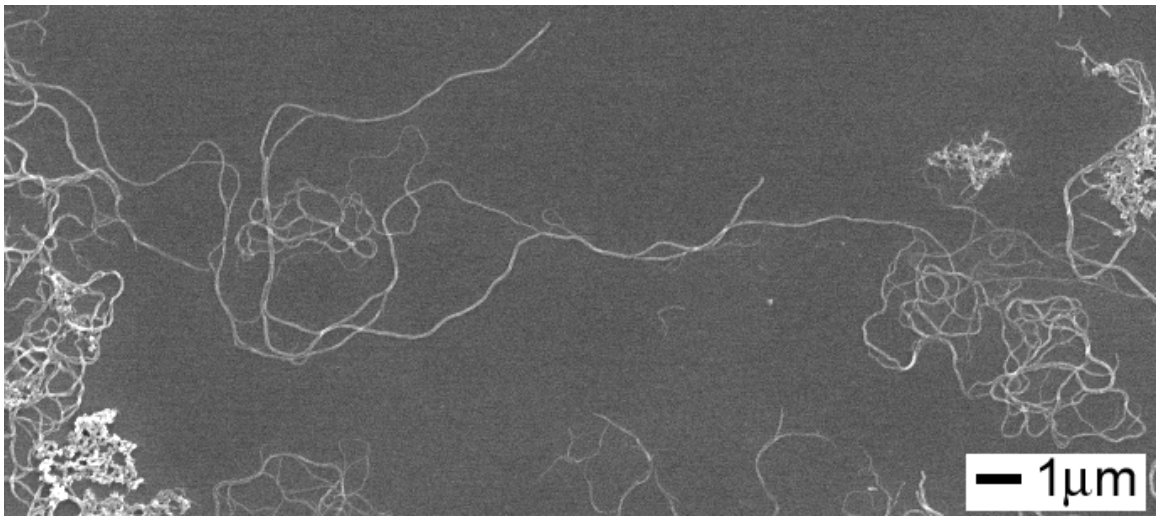
Supporting Figure 8. a)-c) Scanning electron micrograph (SEM) of polyaniline-$HClO_4$ nanofibers prepared using dialysis tubing with MWCO of 3500. (c) Isolated single nanofibers. d)-e) Transmission electron micrograph (TEM) of polyaniline-$HClO_4$ nanofibers (from same sample as (a) – (c) dispersed in ethanol under ultrasonic bath, and then deposited on copper grid substrate. Polymerization conditions: Spectra/Por3 Dialysis Tubing (MWCO: 3,500; Flat width: 45mm), [$HClO_4$]=1.0M, [aniline]=4.025mmoles/12ml of 1.0M $HClO_4$ (inside the tubing), and [APS]=4.025mmoles/500ml of 1.0M $HClO_4$ (outside the tubing) in ice bath.



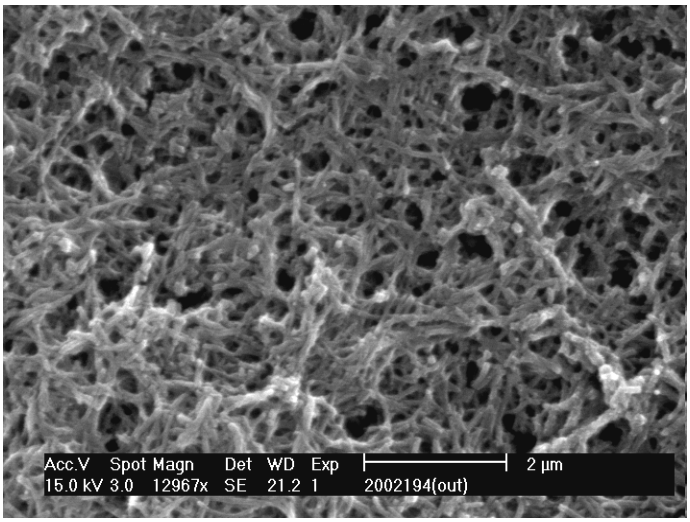
Supporting Figure 9. FT-IR spectrum of polyaniline-CH_3SO_3H nanofibers. (five major vibration bands: 1574, 1490, 1294, 1132 and 796 cm^{-1})



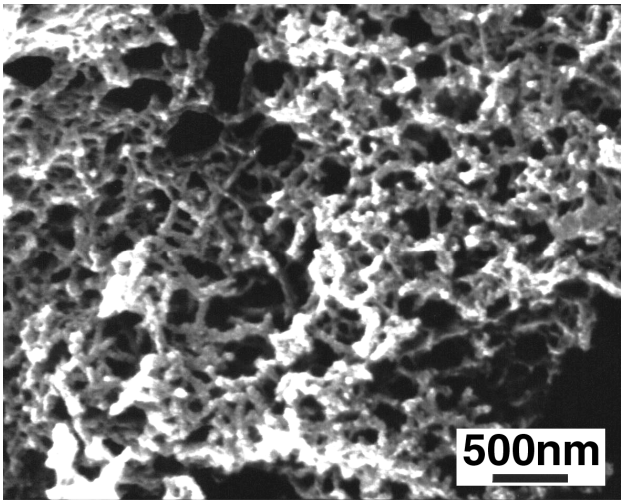
Supporting Figure 10. Scanning electron micrograph (SEM) of polyaniline-$HClO_4$ nanofibers synthesized by PMCP at room temperature using dialysis tubing with MWCO of 3,500. The precipitates were collected a)-b) inside dialysis tubing and c)-d) outside dialysis tubing, respectively.



Supporting Figure 11. Scanning electron micrograph (SEM) of ultra long polyaniline nanofibers prepared by porous membrane controlled polymerization. Polymerization conditions: Spectra/Por Dialysis Tubing (MWCO: 15k; Flat width=16mm), [aniline] = 1.61mmoles/3ml of 1.0M CH_3SO_3H (inside the tubing) and [APS] = 0.8mmoles/200ml of 1.0M CH_3SO_3H (outside the tubing), temperature = ~24 °C, reaction time = 24h and without disturbance.



Supporting Figure 12. Scanning electron micrograph (SEM) of sulfonated polyaniline nanofibers prepared by porous membrane controlled polymerization. Polymerization conditions: Spectra/Por Dialysis Tubing (MWCO: 12k-14k; Flat width=25mm), [aniline] = 1.61mmoles/5ml of 1.0M HCl (inside the tubing), and [metanilic acid] = 32.2mmoles and [APS] = 0.8mmoles/200ml of 1.0M HCl (outside the tubing), temperature = ~24 °C, reaction time = 24h and without disturbance.



Supporting Figure 13. Scanning electron micrograph (SEM) of poly (*o*-toluidine) nanofibers prepared by porous membrane controlled polymerization. Polymerization conditions: Spectra/Por Dialysis Tubing (MWCO: 12k-14k; Flat width=25mm), [HCSA] = 0.2M, [*o*-toluidine] = 1.87mmoles/5ml of 0.2M HCSA (inside the tubing) and [APS] = 0.8mmoles/200ml of 0.2M HCSA (outside the tubing), Temperature = ~24 °C, reaction time = 24h and without disturbance.