

Porous Carbon and Carbon/Metal Oxide Microfibers with Well-Defined Pore Structure and Interface

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Supporting Information

Experimental details

Materials. Methacryloxypropyltrimethoxysilane (MPS), potassium persulfate (KPS), ammonium hydroxide, tetraethyl orthosilicate (TEOS), 80 wt% zirconium butoxide/1-butanol solution, titanium butoxide (97%), and polyoxyethylene(4)lauryl ether (Brij 30) were purchased from Sigma-Aldrich and used without further purification. Acrylonitrile (AN) was purchased from Sigma-Aldrich and the inhibitor within AN was removed by inhibitor remover obtained from Sigma-Aldrich. [Octylphenoxy]polyethoxyethanol (Nonidet P40 Substitute) was purchased from USB Corporation (Cleveland, OH) and used without further purification. Water was purified using a Milli-Q system (Millipore).

Synthesis of SiO₂ nanoparticles and surface modification. The silica particles with diameter in the range of 100-300 nm were synthesized by the well-known Stöber procedure. Typically, to prepare ~200 nm silica particles, 2 mL of ammonium hydroxide (14 mol/L) was dissolved in 25 mL of water. The solution was stirred for 10 min and poured into a glass beaker containing 6 mL of TEOS and 70 mL of ethanol, followed by stirring for 2 h. The silica nanoparticles with diameter in the range of 50-100 nm were synthesized by a reverse emulsion approach. Typically, 2 mL of P40 was dissolved in 8 mL of cyclohexane, followed by adding 1 mL of ammonium hydroxide, and stirred for 1 h to form a transparent reverse microemulsion. Lastly, 3 mL of TEOS was added and stirred overnight at room temperature. The silica nanoparticles were collected by filtration and calcined at 550°C to remove P40. To functionalize the silica particles, the desired amount of the alkaline nanoparticle dispersion was directly mixed with 0.2-0.3 mL MPS at room temperature and stirred for 24 h to ensure covalent bonding. The functionalized silica particles were cleaned by centrifugation and re-dispersed in water.

Synthesis of SiO₂@ZrO₂ and SiO₂@TiO₂ core/shell nanoparticles and surface modification. To coat a layer of zirconia or titania on the silica particles, 0.36 g of silica particles

were dispersed in 25 mL of ethanol containing 0.125 mL of 4 wt% Brij 30 aqueous solution and stirred for 30 min, followed by adding 0.45 mL of 80 wt% zirconium butoxide/1-butanol solution or 0.72 mL of titanium butoxide, and continued stirring overnight. The products were collected by centrifugation and re-dispersed in 25 mL of water for aging. The aging step was carried out at room temperature for 2-24 h (typically, zirconia, 24 h; titania, 2 h). The products were then calcined at 800 °C under air for 6 h for the crystallization of the hydrated zirconia present in the shell into the oxide (for titania, 450 °C). After calcination, the particles were dispersed in a water/ammonium hydroxide/ethanol mixture solution (vol ratio: 25:2:70) for surface modification. 0.1 mL MPS was added at room temperature and stirred for 24 h to ensure successful grafting.

Synthesis of $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2$ core/shell nanoparticles. $\gamma\text{-Fe}_2\text{O}_3\text{@SiO}_2$ core/shell nanoparticles were prepared according to previous literature method (Yi, D. K.; Lee, S. S.; Papaefthymicu, G. C.; Ying, J. Y. *Chem. Mater.* **2006**, 18, 614).

Synthesis of $\text{SiO}_2\text{@PAN}$ and $\text{SiO}_2\text{@MO@PAN}$ core/shell particles. The inorganic/polymer core/shell particle synthesis was carried out by a conventional emulsion polymerization, as described elsewhere (Karg, M.; Pastoriza-Santos, I.; Liz-Marzan, L. M.; Hellweg, T. *ChemPhysChem* **2006**, 7, 2298.). Typically, 0.1 g of MPS-functionalized inorganic particles dispersed in 100 mL of Milli-Q water was prepared in a three-neck flask equipped with a reflux condenser and a magnetic stirrer. The solution was heated to 40 °C and kept under a nitrogen atmosphere to remove oxygen. 1.33 mL of acrylonitrile (AN) was then added and the mixture was then heated to 75 °C. The initiator, 10 mg of potassium persulfate (KPS) dissolved in 1 mL of Milli-Q water, was added after 1 h of intense stirring at 75 °C under nitrogen atmosphere to start the polymerization. The polymerization proceeded for overnight at 75 °C. The white and strongly turbid solution was then cooled to room temperature and the prepared core/shell particles were cleaned by centrifugation and re-dispersed into water.

Freezing $\text{SiO}_2\text{@PAN}$ and $\text{SiO}_2\text{@MO@PAN}$ core/shell particles into fibrous structures. The inorganic/polymer core/shell particles were dispersed in a 0.1 wt% PVA (M.W.~72000) aqueous solution and diluted to 0.1-0.5 wt%, followed by freezing at a -80 °C cold bath. Afterwards, the ice was sublimed by freeze drying, such that a scaffold which consisted of interwoven fiber bundles was produced. The produced fibers were stabilized under oxidative atmosphere to avoid softening and melting of carbon fibers at higher temperatures, which was accomplished by heating the fibers in air to 200 °C for 1 h. A pyrolysis process was then carried out to carbonize the fibers at 800 °C under argon atmosphere, followed by removal of silica cores with hydrofluoric acid or concentrated alkali (e.g. 10 M NaOH) to create porous carbon fibers.

Characterizations. Transmission electron microscopy (TEM) images were obtained using a JEOL 2010 microscope operated at 200 kV. Scanning electron microscopy (SEM) studies were performed on an FEI XL40 Sirion FEG microscope. Powder XRD patterns were collected on a Scintag PADX diffractometer with Cu K α radiation (45 kV, 35 mA). Nitrogen sorption measurements were performed on a TriStar 3000 system.

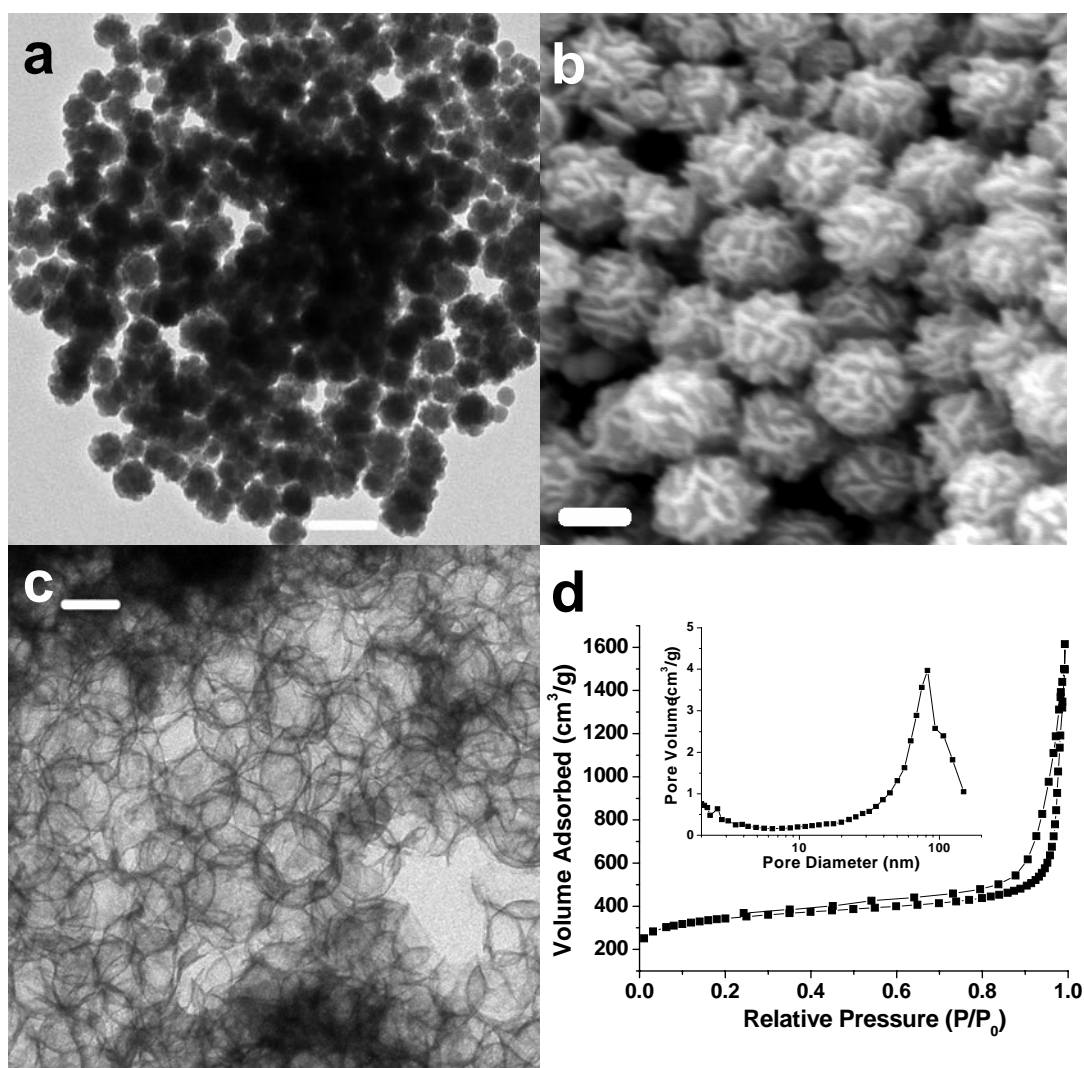


Figure S1. (a-c) TEM and SEM micrographs of SiO₂@PAN particles and hollow carbon capsules templated from ~200 nm silica particles, (d) nitrogen adsorption/desorption isotherms and the corresponding pore size distribution of porous carbon capsules templated from ~80 nm silica nanoparticles. The BET surface area and pore volume are measured to be 1176.8 m²/g and 2.23 cm³/g, respectively. Scale bars: (a) 500 nm; (b, c) 200 nm.

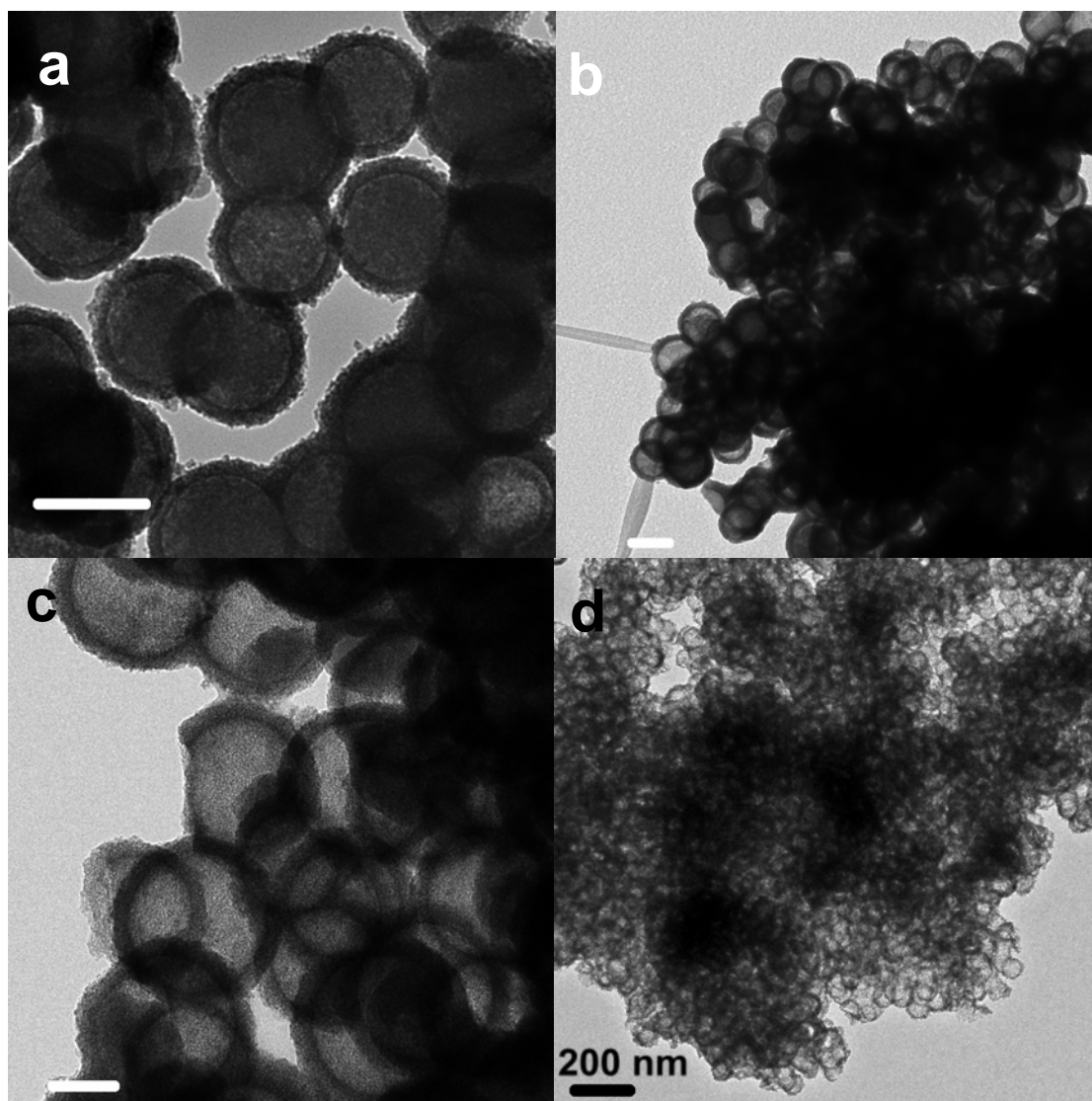


Figure S2. TEM micrographs of (a) $\text{SiO}_2@\text{ZrO}_2@\text{C}$ particles, (b,c) hollow $\text{ZrO}_2@\text{C}$ capsules templated from ~ 200 nm silica particles, (d) hollow $\text{ZrO}_2@\text{C}$ capsules templated from ~ 80 nm silica nanoparticles. Scale bars: (a, b) 200 nm, (c) 100 nm.

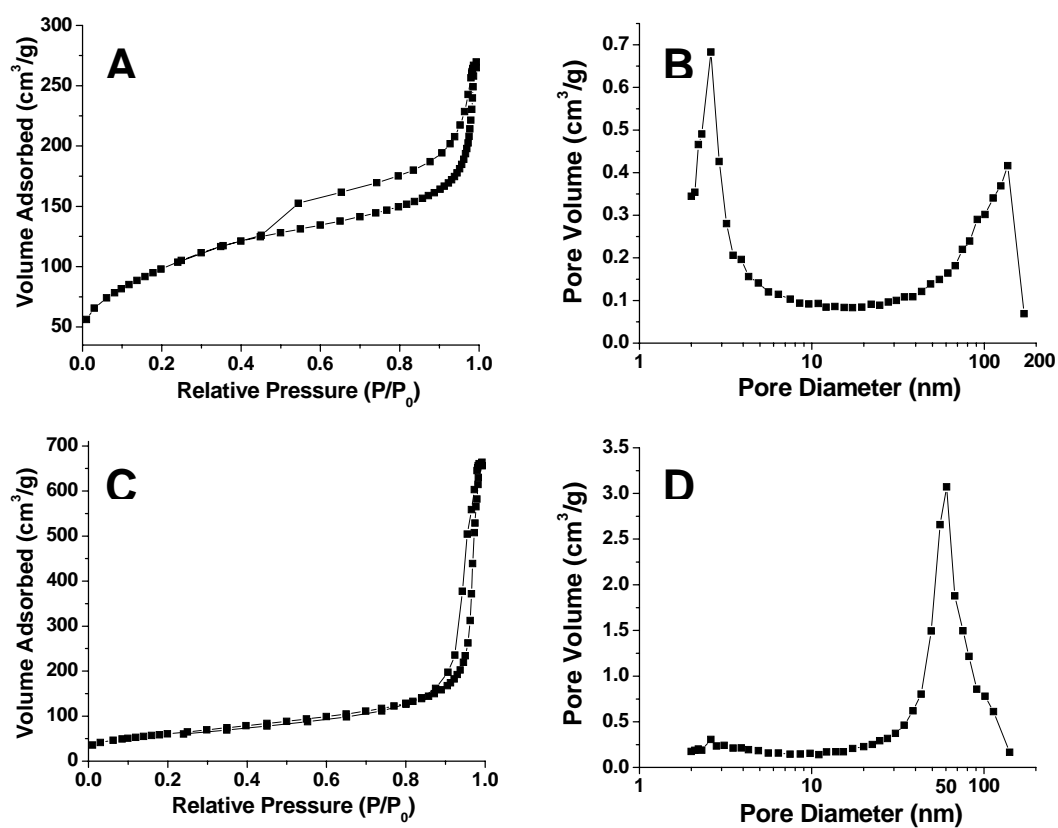


Figure S3. Nitrogen adsorption/desorption isotherms and the corresponding pore size distributions of (A, B) hollow $\text{ZrO}_2@\text{C}$ capsules templated from ~ 200 nm silica particles (BET surface area: $351.4 \text{ m}^2/\text{g}$, pore volume: $0.39 \text{ cm}^3/\text{g}$) and (C,D) hollow $\text{ZrO}_2@\text{C}$ capsules templated from ~ 80 nm silica nanoparticles (BET surface area: $216.5 \text{ m}^2/\text{g}$, pore volume: $1.04 \text{ cm}^3/\text{g}$).

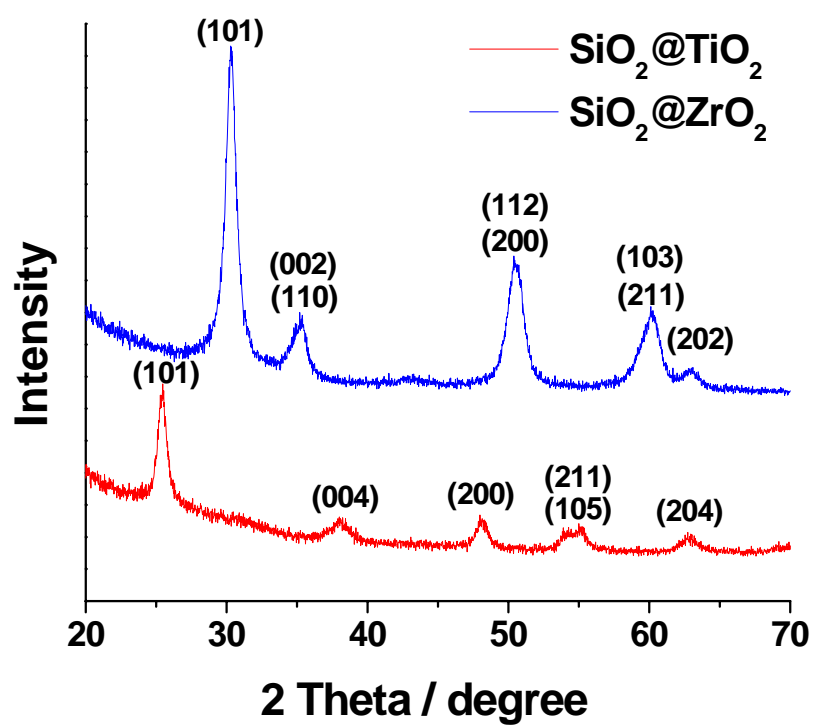


Figure S4. Wide angle X-ray diffraction patterns of $\text{SiO}_2@\text{TiO}_2$ and $\text{SiO}_2@\text{ZrO}_2$ particles.

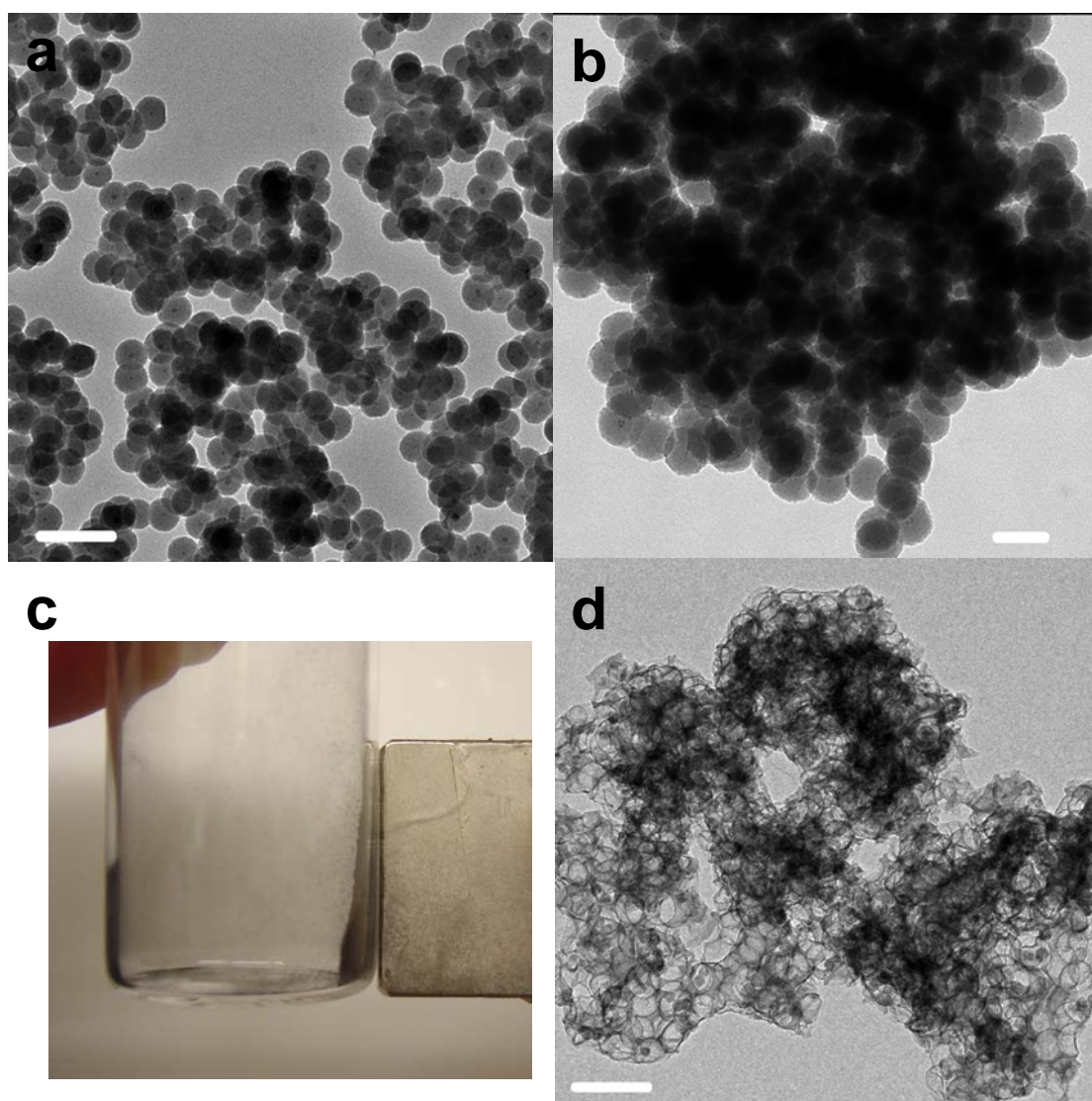


Figure S5. TEM micrographs of (a) $\gamma\text{-Fe}_2\text{O}_3@\text{SiO}_2$ particles, (b) $\gamma\text{-Fe}_2\text{O}_3@\text{SiO}_2@\text{C}$ particles, and (d) hollow $\gamma\text{-Fe}_2\text{O}_3@\text{C}$ capsules. (c) digital image of hollow $\gamma\text{-Fe}_2\text{O}_3@\text{C}$ capsules responding to external magnetic field. Scale bars: (a, d) 200 nm, (b) 100 nm.

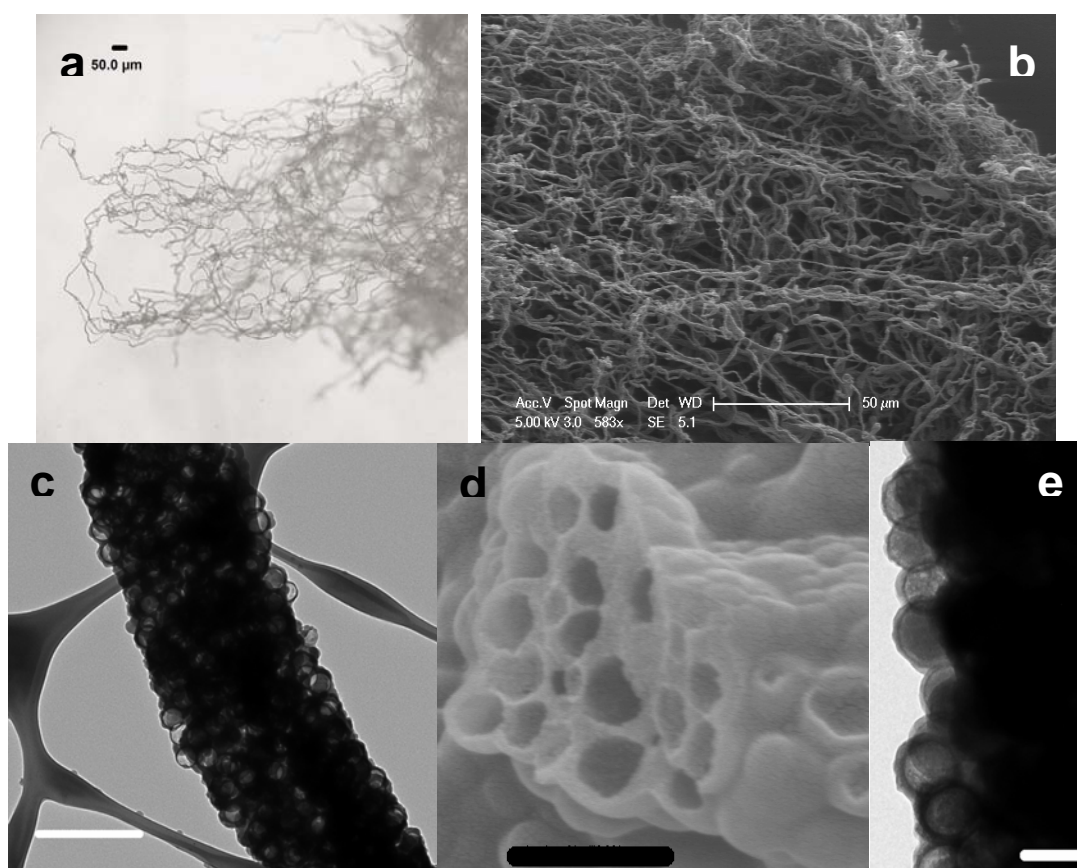


Figure S6. (a) digital image, (b, d) SEM micrographs and (c) TEM micrograph of porous carbon fibers templated from ~200 nm silica particles. (e) TEM micrograph of porous carbon/ZrO₂ fibers. Scale bars: (a, b) 50 μm, (c-e) 200 nm.

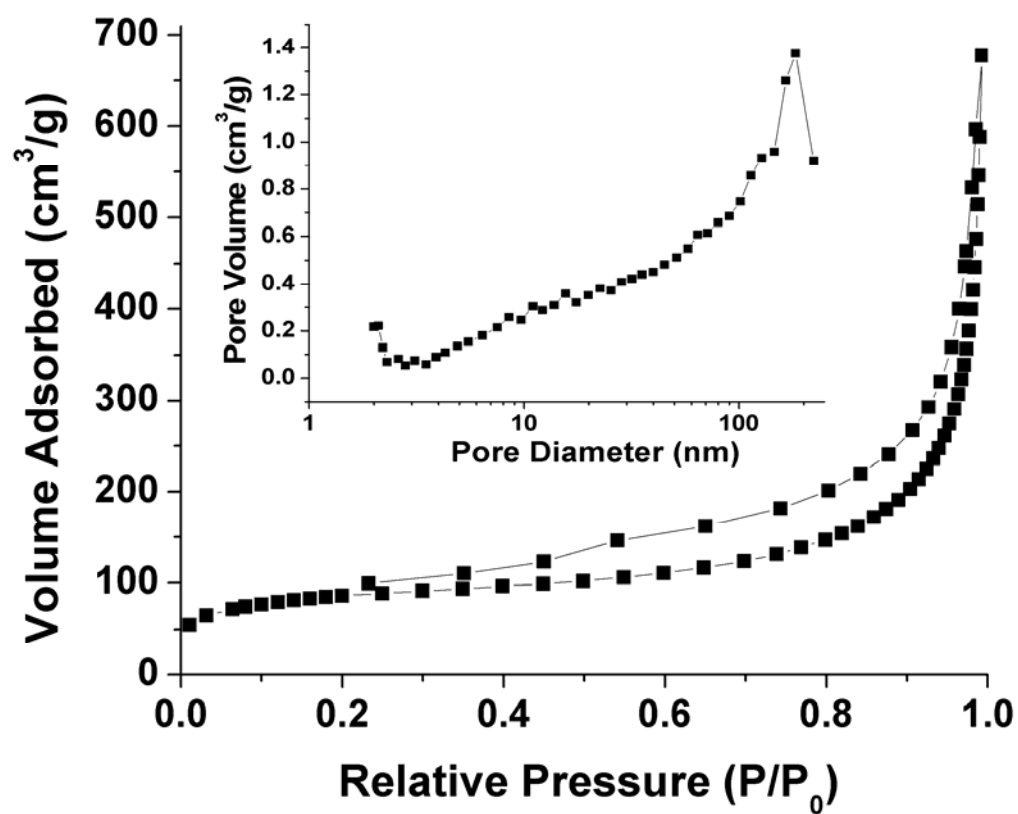


Figure S7. Nitrogen adsorption/desorption isotherm and the corresponding pore size distribution of porous carbon fibers templated from ~200 nm silica particles.