A Novel Route to Polymeric Sub-micron Fibers and Their Use as Templates for Inorganic Structures

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Supporting Information

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Experimental Details

Chemical and reagents

Poly(vinyl alcohol) (PVA) (80 % hydrolyzed, Mw 9000-10000), sodium carboxymethyl cellulose (SCMC), alginic acid sodium salt (NaAlg), titanium(IV) isopropoxide (97%, $Ti(OiPr)_4$), and PVA (99+% hydrolyzed, Mw 89,000-98,000) were purchased from Sigma-Aldrich. Rhodamine B was bought from Fisher Scientific. TiO_2 P25 (Degussa) was purchased from Lawrence Industries. Distilled water and normal GPR solvents and $FeCl_3$ (BDH) were used as received.

Preparation of polymer sub-micron fibers and inorganic structures

Aqueous dilute polymer solutions at different concentrations were firstly prepared. The polymer solutions in a shallow glass beaker were frozen in liquid nitrogen by slowly touching and then immersing in liquid nitrogen. The frozen samples were freeze-dried in a freeze drier (LyoLab 3000, Heto) for 48 h. A range of polymeric sub-micron fibers were produced after the freeze-drying process.

SCMC sub-micron fibers prepared from 0.1 wt % SCMC (Mw 250,000) was immersed in 0.07 g/ml $FeCl_3$ solutions for 6 h. The resulting yellow composite was taken out, filtered using a funnel, and completely rinsed with a large amount of water. The composite was placed on the tissue paper in air at room temperature overnight and then calcined in a furnace (Carbolite, CWF1200) to produce Fe_2O_3 nanofibers. The calcining condition: heating at 1 ^{0}C min^{-1} in air to 600 ^{0}C, kept hold for 480 minutes, and then cool down to room temperature.

PVA sub-micron fibers obtained from 0.1 wt % PVA (Mw 89,000-98,000) and SCMC sub-micron fibers from 0.1 wt % SCMC (Mw 250,000) were immersed in the $Ti(O\textit{i}Pr)_4$ in 2-propanol solution (0.3 g 2-propanol + 1 ml $Ti(OiPr)_4$) for 6 h. After filtering and rinsing with 2-propanol, the soaked materials were left in air at room temperature overnight to allow the sol-gel process to take place. The composites were calcined with the procedure of heating at 1 ^{0}C min^{-1} in air to 600 ^{0}C, kept hold for 480 minutes, and then cool down to room temperature.

The microanalysis data for the calcined inorganic fibers are shown below:

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	C (%)	H (%)	N (%)
Fe_2O_3	0.14	0	0
TiO_2 (from PVA)	0.20	0	0
TiO_2 (from SCMC)	0.76	0.15	0

Characterization

Morphologies of the fibers were observed using a Hitachi-S4800 SEM equipped with a STEM detector and an EDX detector (INCA 7200, Oxford Instrument). For SEM imaging, the samples were adhered to SEM studs and coated with gold using a sputter-coater (EMITECH K550X) for 3 min at 40 mA. Polymer sub-micron fibers observed by the STEM detector were prepared by dropping the fibers suspension onto the TEM grid. Surface area and pore size distribution were measured using an ASAP 2020 nitrogen adsorption analyzer. PXRD data were collected on a Panalytical X'Pert Pro Multi-Purpose Diffractometer in high-throughput transmission geometry. The Cu anode was operated at 40 kV and 40 mA. Patterns were collected for 16 hours (16 x 1 h scans) from 2 – 80 deg 2 theta with a step size of 0.006 deg.

Assessing the photocatalytic activity of TiO_2 nanofibers

10 mg TiO_2 nanofibers made from PVA and SCMC nanofibers or P25 were firstly dispersed into the 10 ml aqueous Rhodamine B solution at the concentration of 10 mg/L. The suspension was stirred for 20 min in dark to approach adsorption and desorption equilibrium and then the suspension was continuously stirred under UV light (254 nm, 4W). 1 ml of the suspension was taken out periodically and centrifuged for UV measurement and then put back into the reaction mixture. The concentration change of Rhodamine B in the solution was monitored using a UV plate reader (μQuant, Bio-Tek instrument Inc.). The absorbance at 550nm was used to obtain the concentrations for Rhodamine B and calculate its degradation rate.

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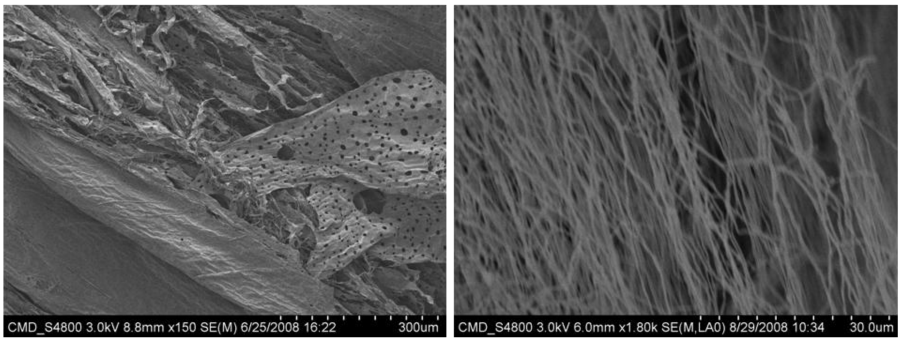
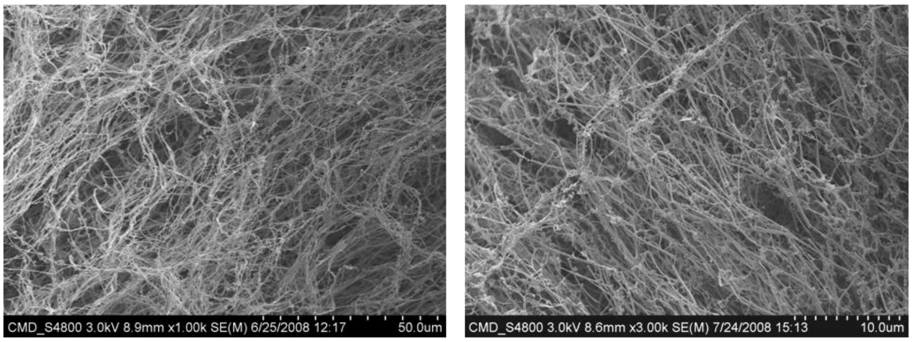


0.5 wt % SCMC (250K)   0.2 % SCMC (250K)



0.1 wt % SCMC (250K)   0.05 wt % SCMC (250K)

Figure S1. Porous structures of aqueous SCMC (Mw 250K) solutions with different concentrations frozen in liquid nitrogen and then freeze dried. Freezing dilute solutions led to the formation of nanofibers.

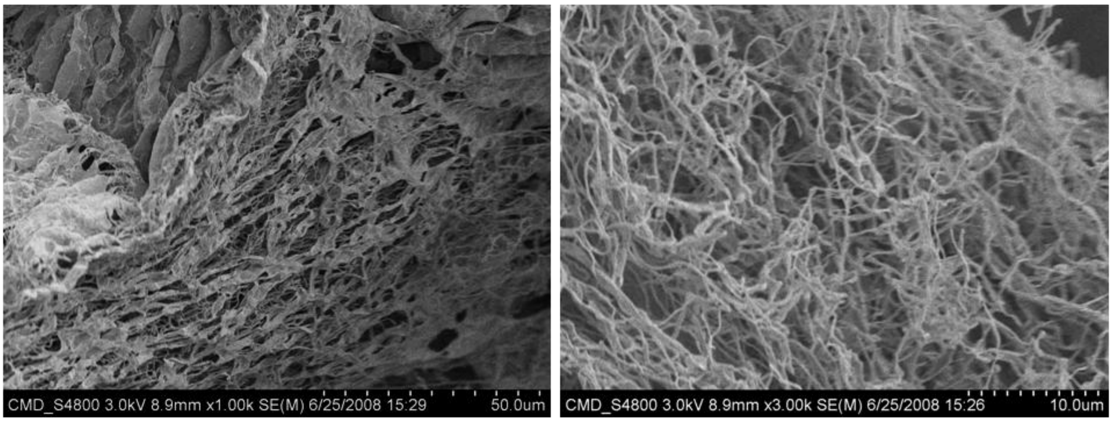


Figure S2. Porous structure of PVA (Mw 89-98K) processed from the 0.5 wt % aqueous solution. Part of it was nanofiber structure (image on the right).

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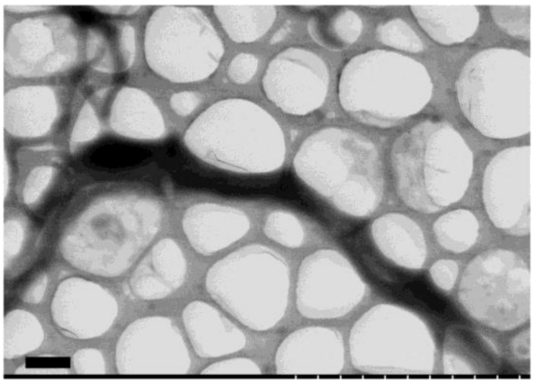

Figure S3. STEM image of a PVA nanofiber obtained from freezing 0.1 wt % PVA (Mw 89,000-98,000) in liquid nitrogen. Scale bar: 600 nm.

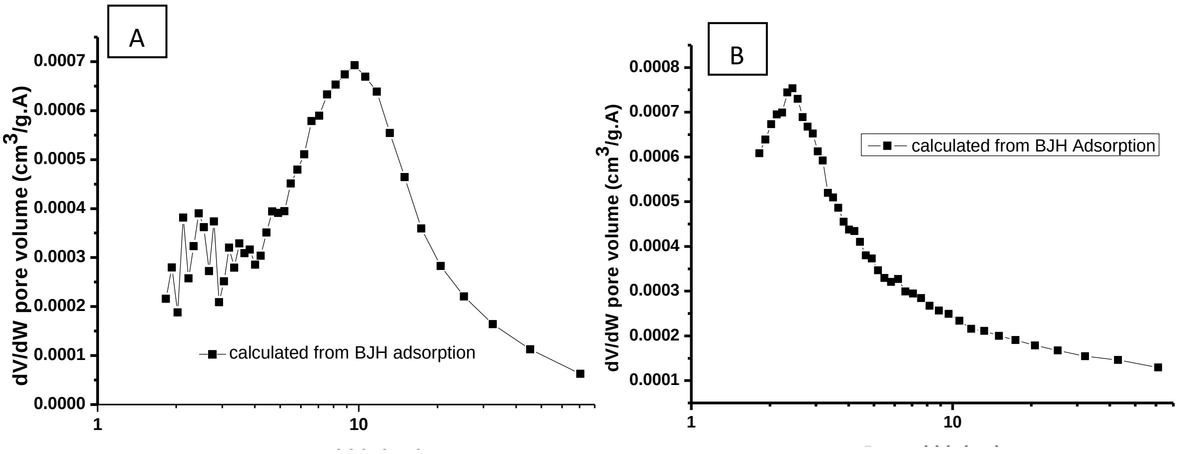

Figure S4. (A) Pore size distribution of titania nanofibers made using PVA as template. This material has a BET surface area of 53.20 $m^2.g^{-1}$ and a mesopore size distribution around 10 nm. (B) Pore size distribution of titania powders P25 (Degussa). This commercial product exhibits a surface area of 52.80 $m^2.g^{-1}$ (measured by us) or 50 ±15 $m^2.g^{-1}$ (data from the provider).

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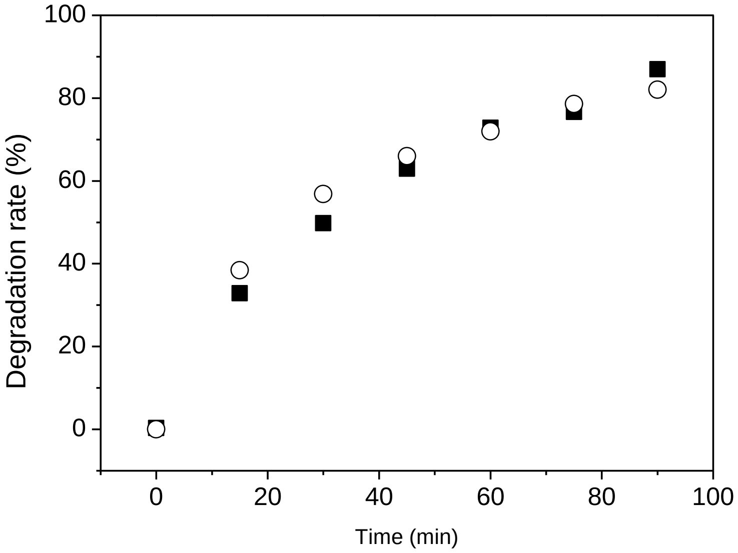

Figure S5. Degradation rate of Rhodamine B in water under UV irradiation (254 nm) using titania as the photocatalyst: TiO_2 nanofibers (○) and P25 (■). The initial concentration of Rhodamine B was 10 mg/L.

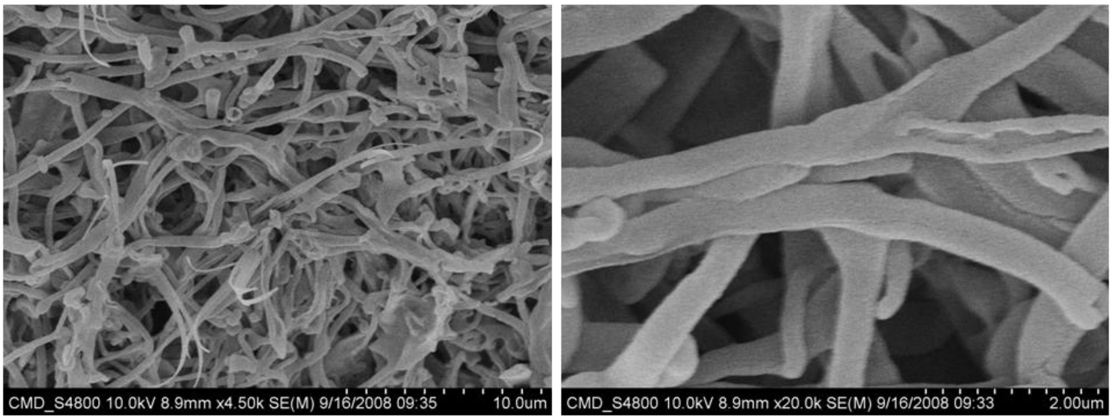

Figure S6. Titanium oxide nanofibers made with SCMC (Mw 250K) nanofibers as templates.

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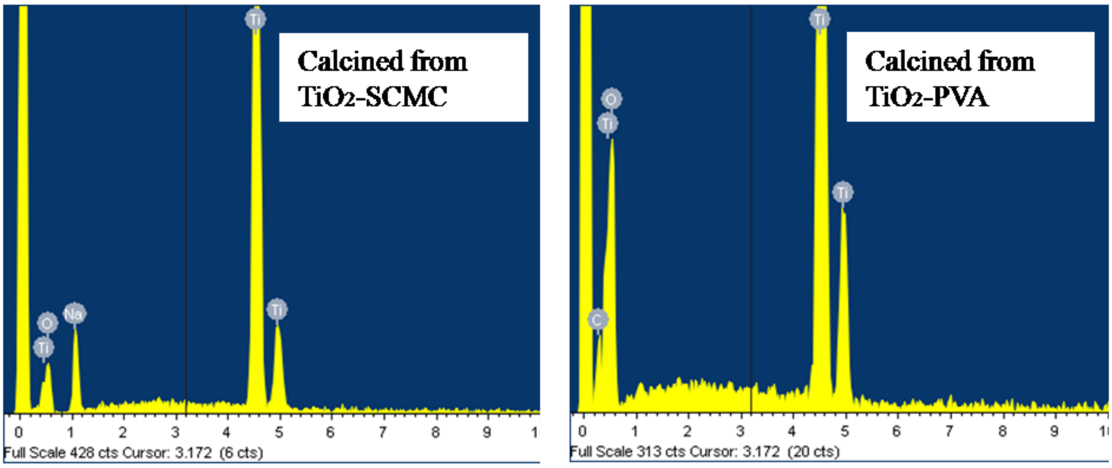

Figure S7. Element analysis of titanium oxide nanofibers made from SCMC and PVA, as measured by energy dispersive X-ray (EDX) microanalysis. The presence of Na from SCMC-made nanofibers is clearly seen with a weight percentage of 11.42 %. The first strong unlabelled signals are from the Beryllium (Be) internal standard.

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