Supporting Information

Bacterial cellulose-templated synthesis of free-standing silica nanotubes with three-dimensional network structure

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EXPERIMENTAL SECTION

1.1. Preparation of BC pellicles

Briefly, the bacterial strain, *Acetobacter xylinum* X-2, was grown in the culture media containing 0.3 wt% green tea powder (analytical grade) and 5 wt% sucrose (analytical grade) for 7 days. The pH of the medium was adjusted to 4.5 by acetic acid. BC pellicles were purified by soaking in deionized water at 90 °C for 2 h followed by boiling in a 0.5 M NaOH solution for 15 min. The pellicles were then washed with deionized water several times and soaked in 1 wt% NaOH for 2 days. After rinsing with deionized water until neutrality, the BC pellicles were finally freeze-dried to obtain BC aerogels.

1.2. Preparation of silica-coated BC nanofibers

In a typical experiment, a BC aerogel (approximately 25 mg) was soaked in absolute ethanol for 60 min to remove the absorbed water and followed by immersion in a known quantity (4.5 ml) of tetraethylorthosilicate (TEOS) which was diluted with 10 ml of ethanol for 24 h to allow TEOS polymerization. Afterwards, the resultant BC aerogel coated with TEOS was taken out, rinsed twice with absolute ethanol, and then soaked in ethanol/water 9:1 for 24 h to allow hydrolysis and polycondensation in a closed container set at room temperature (25 °C) and -30 °C, respectively, and the resultant samples, denoted as $SiO_2/BC+25$ and $SiO_2/BC-30$, respectively, were washed three times with deionized water. The silica-coated BC samples were dried by lyophilization prior to calcination.

1.3. Preparation of silica nanotubes

To remove the templates, the silica-coated BC (including SiO_2/BC+25 and SiO_2/BC-30) samples were calcined in an electrically heated furnace and heated from room temperature to 500 °C at a heating rate of 1 °C /min to avoid the collapse of 3D nanotube network. After maintaining the peak temperature (500 °C) for 6 h the samples were cooled to room temperature with a cooling rate of 5°/min, resulting in two different silica nanotubes, SiO_2+25 and SiO_2-30, derived from SiO_2/BC+25 and SiO_2/BC-30, respectively.

1.4. Characterizations

The silica-coated BC and silica nanotube samples were characterized by scanning electron microscopy (SEM, Nova Nanosem 430) from which the fiber diameter was determined by measuring at least 100 randomly selected fiber segments, transmission electron microscopy (TEM, Tecnai G2F-20) at an acceleration voltage of 200 kV, and X-ray diffraction (XRD, Rigaku D/Max 2500 v/pc) with Cu K_α radiation. Thermogravimetric analysis (TGA) was performed on a simultaneous TGA/DSC analyzer (STA449F3) from 30 to 800 °C at a heating rate of 10 °C/min in air. Fourier transformed infrared spectroscopy (FTIR) analysis was conducted by Shimadzu IRPrestige-21 (Japan) and FTIR spectra were recorded in a spectral range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. The Brunauer–Emett–Teller (BET) surface area of silica nanotubes was evaluated from nitrogen adsorption isotherms at 77 K using a surface area analyzer (NOVA 2200e). The fiber diameter was measured from SEM images. Compression tests were performed using a micro electromagnetic fatigue testing machine (IBTC-300, Tianjin Care Measure & Control Co., Ltd., Tianjin,

China). The strain rate was maintained at 0.2 mm min^{-1}. Photoluminescence (PL) measurement was carried out on a Horiba Jobin Yvon Fluorolog3-21 Fluorescence Spectrometer at room temperature using two different excitation sources (325 and 375 nm lights).
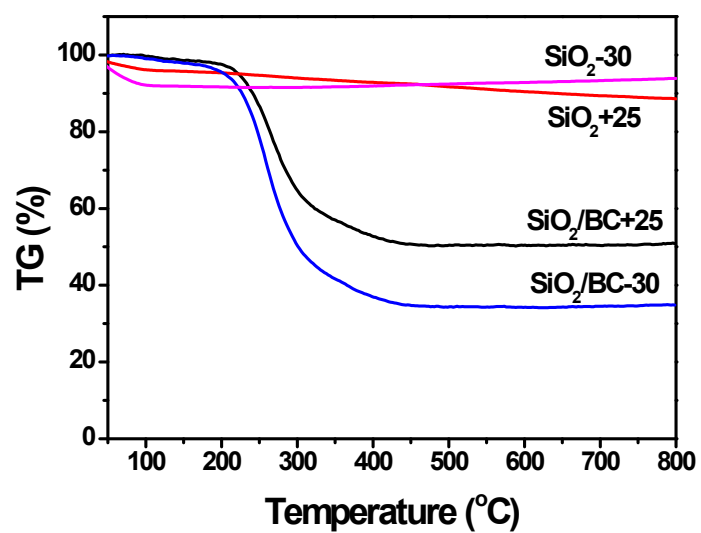
Table S1. Pore structure parameters of two different silica nanotubes

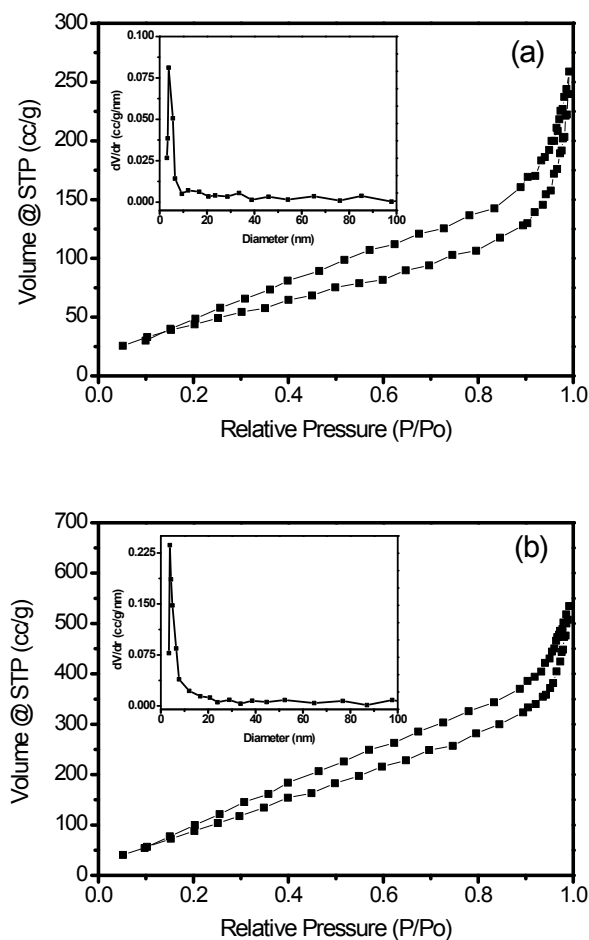| Samples	BET surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore diameter (nm)
SiO$_2$+25	177.1	0.4005	3.810
SiO$_2$-30	451.0	0.8267	3.819
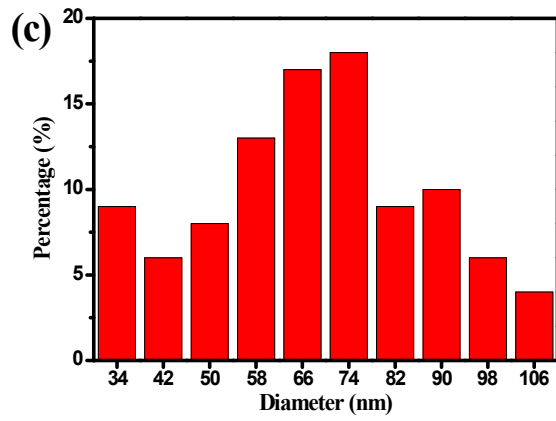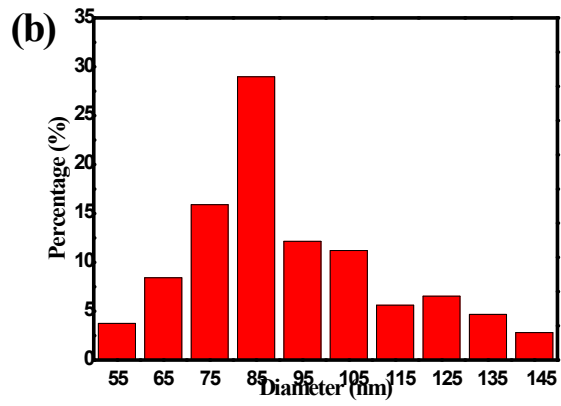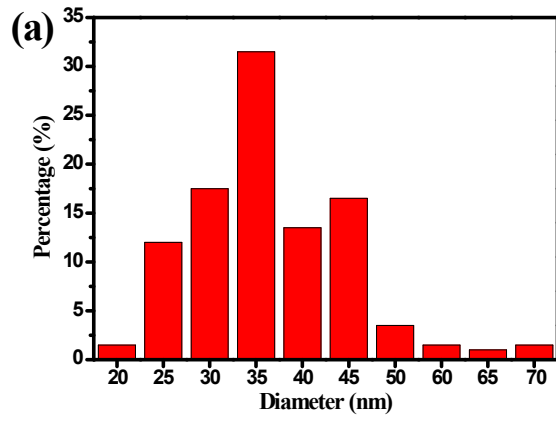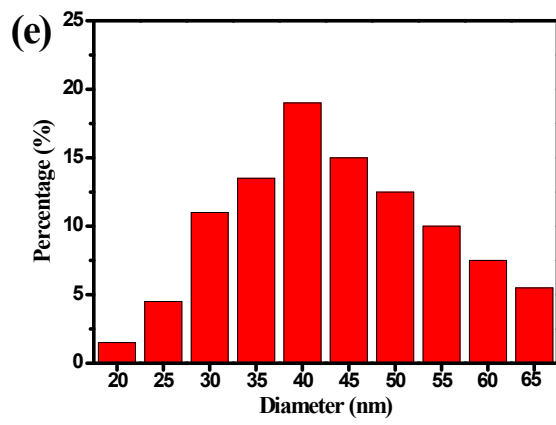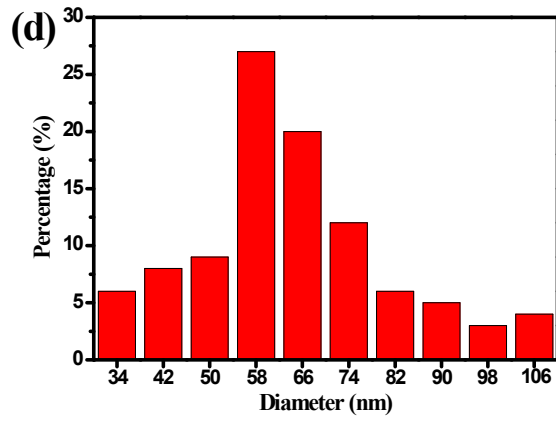
Figure S1. Fiber diameter distribution of pristine BC (a), $SiO_2/BC+25$ (b), SiO_2/BC-30 (c), SiO_2+25 (d), and SiO_2-30 (e).

Figure S2. TGA curves of silica-coated BC and silica nanotubes.

Figure S3. N_2 adsorption–desorption isotherms and pore size distribution (insets) of SiO$_2$+25 (a) and SiO$_2$-30 (b) nanotubes.

It can be seen that both SiO$_2$+25 and SiO$_2$-30 nanotubes show a typical type IV isotherm with type H3 hysteresis loop according to BDDT classification,[4] indicating the presence of mesopores (2–50 nm). A similar isotherm has been recently reported by Chattopadhyay and co-workers for TiO$_2$ nanofibers with mesopores.[5] Moreover, the observed hysteresis loop approaches P/P$_0$= 1, suggesting the presence of macropores (> 50 nm).[6] As shown in Table S1, the BET surface area of SiO$_2$+25 and SiO$_2$-30 calculated from N$_2$ adsorption/desorption isotherms is 177.1 and 451.0 m^2 g^{-1},

respectively, and the pore volume is determined as 0.4005 and 0.8267 cm^3 g^{-1}, respectively. These values are comparable to those of previously reported silica nanotubes.[7, 8] The pore size distribution curves calculated using the Barrett–Joyner–Halenda (BJH) equation from the adsorption branch of the isotherm are displayed in Figure S5 as insets. SiO_2+25 and SiO_2-30 show a peak at 3.810 and 3.819 nm, respectively.

References

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