Supplementary Information

Thoroughly mesoporous TiO$_2$ nanotubes prepared by foaming agent assisted electrospun template for photocatalytic applications

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Experimental Section

Materials:
The raw materials of PVA (degree of polymerization: 1500, Wako Pure Chemicals Ind., Ltd., Japan.), titanium isopropoxide (TTIP, Wako Pure Chemicals Ind., Ltd., Japan.), diisopropyl azodiformate (DIPA, Wako Pure Chemicals Ind., Ltd., Japan) were commercially available and used directly without further purification. The solvents used in this paper are distilled water and absolute ethyl alcohol, respectively. P25 (~45 m²/g) was obtained from Nippon Aerosil Co., Ltd.

Experimental information
Firstly, the PVA nanofiber template was electrospun as the following conditions. 10 wt% PVA aqueous solution was prepared by dissolving PVA in distilled water. The electrospinning solution was loaded into a plastic syringe (2 mL) equipped with a needle. The solution extrusion rate was 1.02 mL/h. The distance and voltage applied between the needle tip and the collector were set at 15 cm and 15 kV, respectively. Secondly, the as-spun PVA nanofibers were immersed in absolute ethanol containing 20 wt% titanium isopropoxide (TTIP) and 10 wt% foaming agent diisopropyl azodiformate (DIPA) for 30 minutes at room temperature. In this process no stirring was needed. After that the composite nanofibers were taken out, washed by absolute ethanol for several times to remove the residual reactants and then dried under room temperature for 20 min. Finally the composite nanofibers were calcined at 500 °C (heating rate at 4 °C/min) for 2 h to obtain the mesoporous TiO₂ nanotubes. For comparison, the controlled solid TiO₂ nanotubes were obtained the same as the above processes without adding DIPA. The resultant mesoporous TiO₂ and solid TiO₂ nanotubes were marked as Sample NT1 and Sample NT2, respectively.

Characterization
The as-prepared products were characterized with field emission scanning electron microscopy (FESEM, Zeiss Ultra55, Germany), X-ray powder diffraction (XRD, Rigaku Miniflex II, Japan) using a CuKα with a Ni filter(30 kV, 15 mA) and high-resolution transmission electron microscopy (HRTEM, JEM-2010F, JEOL, Japan). The porous properties of the as-prepared mesoporous nanofibers were characterized using N₂ adsorption at -196 °C on a specific surface area and porosity analyzer (Micromeritics, TRYSTAR 3000, Japan). The thermal behaviors of the as-spun precursors were analyzed
by a TG-DTA thermoanalyzer (Shimadzu DTG-60, Japan) with a heating rate of 10 °C/min in air.

**Photocatalytic performance evaluation**

The photodegradation of methylene blue in water was used to evaluate the photoactivity of the samples as prepared through different methods, in our experiment, a consistent dosage of 25 mg samples were dispersed into 25 ml methylene blue solution with the initial concentration of 10 mg/L. The photodegradation experiment was carried out under the irradiation of extra-high pressure Hg lamp (125 W). Three milliliters of test liquid was taken from this solution and fed in a quartz cell. The concentration of methylene blue in solutions were monitored and analyzed by measuring the absorbance at 665nm wavelength using UV-vis spectrometer at given irradiation time intervals.
Figure S1 (a) The as-spun PVA nanofibers and (b) the DIPA/Ti-precursor/PVA nanofibers
Fig. S2 The element mappings of (a) Ti, (b) O and (c) N within a single DIPA/Ti-precursor/PVA nanofiber under SEM.
Fig. S3 HRTEM images of (a) the mesoporous TiO\textsubscript{2} nanotube (Sample NT1, Fig. 1e) and (b) solid TiO\textsubscript{2} nanotube (Sample NT2).
Fig. S4 A typical EDS spectrum (a) and the element mappings of (b) Ti and (c) O recorded from a single mesoporous TiO$_2$ nanotube of Sample NT1 under SEM.
Fig. S5 A typical HRTME image of interconnection part of mesoporous TiO$_2$ nanotubes of sample NT1
Fig. S6 Morphologies of the Solid TiO$_2$ nanotubes under different calcination time (a)1h. (b)2h. (c)5h. (d)10h

Fig. S7 A typical SEM image of Sample NT1 (mesoporous TiO$_2$ nanotubes) after photocatalysis for the degradation of MB.