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Electronic Supplementary Information

Flame synthesis of hierarchical nanotubular rutile titania

derived from natural cellulose substance

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Experimental Details

Reagents: Titanium *n*-butoxide $[Ti(O^nBu)_4]$ and methylene blue were purchased from Aldrich. All the solvents were guaranteed reagents and were used without further purification. The water used in all the related experiments was purified by using a Milli-Q Advantage A10 system (Millipore, Bedford, MA, USA) with resistivity higher than 18.2 M Ω cm.

Materials fabrication: Titania nanocoating of natural cellulose substance (common commercial filter paper, quantitative ashless) was realized by means of a surface sol–gel process. Briefly, a piece of filter paper was placed in a suction filtering unit and was cleaned by suction filtration of ethanol (10 mL), followed by drying with air flow for 15 min prior to use. 20 mL of $Ti(O^nBu)_4$ solution (100 mM in toluene–ethanol, v:v = 1:1) was added into the filter funnel, and the first 10 mL of which was slowly suction filtered through the filter paper. The rest solution was left to stand for 3 min to achieve chemical adsorption of the titanium alkoxide on the cellulose nanofibre surface. Then, the remaining 10 mL solution was slowly suction filtered through the filter paper was washed immediately by suction filtration of absolute ethanol (40 mL) to remove the unreacted titanium alkoxide. Subsequently, pure water (20 mL) was allowed to pass through the filter paper to promote hydrolysis and condensation of the titanium alkoxide, and then dried by air flow. Thus an ultrathin titania layer was deposited covering the surface of each cellulose nanofibre of the filter paper (thickness *ca*. 0.5 nm). By repeating the titania deposition cycle *n* times, titania gel films with

desired thickness were formed coating each cellulose nanofibre of the filter paper. The as-prepared titania/filter paper composite sheet was placed in a porcelain crucible, and was burned by gas torch lighter (YZ 829, piezo ignition, butane power), forming the white nanotubular rutile titania material. As a comparison, the as-prepared titania/filter paper composite fabricated by 20 titania thin films deposition cycles was calcined in air at 1000 °C for 2 h (heating rate 2 °C min⁻¹), giving the corresponding rutile titania.

Photodegradation of methylene blue: Degradation of methylene blue in aqueous solution was evaluated by using a XPA photoreactor (Nanjing Xujiang). Typically, the resultant nanotubular rutile titania material (5.0 mg) was broken into small pieces by ultrasonication for 20 s in pure water (20 mL) in a beaker; and then an aqueous solution of methylene blue (10.0 mg L⁻¹, 20 mL) was added. The final concentration of methylene blue in the suspension was 5.0 mg L⁻¹. The resulted suspension was placed in the dark with stirring for 30 min to achieve sufficient adsorption. Then, ultraviolet light irradiation was carried out under stirring with a 300 W high pressure mercury lamp (horizontal lamp-sample distance: ~5 cm). The suspension (1.5 mL) was extracted at a defined time interval of 10 min or 20 min, and was centrifuged at 3,000 rpm for 5min to get clear solution, which was thereafter subjected to UV–vis absorption measurement. The absorbance at 664 nm (π – π * transition of the tricyclic aromatic structure of methylene blue molecule) of each solution was recorded to monitor the changes of the methylene blue concentration with irradiation time.

Characterizations: Specimens for electron microscope examinations were prepared by ultrasonication treatment of the corresponding product in ethanol until homogeneous suspension was obtained. The resulting suspension was then dropped onto silicon wafer or onto carbon-coated copper grid followed by drying in air for field emission scanning electron microscopic (FE-SEM) and transmission electron microscopic (TEM) observation, respectively. FE-SEM images were acquired on a FEI Sirion-100 instrument with EDAX Genesis4000 at an accelerating voltage of 5.0 kV, and the specimens were sputtered with platinum to reduce charging. TEM and the high-resolution transmission electron microscopic (HR-TEM) observations were performed on a Philips CM 200UT microscope operating at an accelerating voltage of 160 kV. Fourier transform infrared

(FT-IR) spectra were measured on a Nicolet Nexus 670 spectrometer using KBr pellets. Powder Xray diffraction (XRD) measurements were conducted on a Philips X'Pert Pro diffractometer with a CuK_a ($\lambda = 0.15405$ nm) radiation source. UV–vis spectra were recorded with a Shimadzu UV-2450 spectrophotometer in the transmission mode for solution samples; and in the diffuse reflectance mode for solid samples using an integrating sphere accessory with BaSO₄ as the reference standard. Nitrogen adsorption–desorption isotherms were obtained at –196 °C with a Micromeritics ASAP 2020 analyzer, the specific surface area was calculated by using the Brunauer–Emmett–Teller (BET) model.



Fig. S1 TEM micrographs of a virgin cellulose nanofibre of the filter paper (a), a titania gel film coated cellulose nanofibre (b), and an anatase titania nanotube that obtained by calcination (at 450 °C in air) of the titania-coated nanofibre (c). Deposition of titania thin film was repeated twenty times for this sample. The titania gel film coating on the cellulose nanofibre is clearly identified by comparing micrographs (a) and (b), and the uniform anatase titania nanotube obtained by removal of the cellulose component (c) further confirms the existing of the titania gel film coating layer.



Fig. S2 FE-SEM micrograph of the bare filter paper used in the current study, showing cellulose microfibers composed of nanofibers. Cellulose is a linear natural polymer of β -(1 \rightarrow 4)-D-glucopyranose, with the formation of the inter- and intra-molecular hydrogen bonds, the polymer chains assemble into fine fibrils (diameters several nanometers) and fibril aggregates (*nanofibres*, diameters tens of nanometers), and further bundle to form randomly cross-linked networks of *microfibres* (diameters in the micrometer level or even larger).



Fig. S3 EDX spectra of the nanotubular rutile titania materials fabricated by flame burning of the as-prepared titania/cellulose composite sheet. The deposition cycle of titania thin films was repeated 20 (a), 10 (b), and 5 times (c), respectively. The Si signals originated from the silicon wafers used to support the specimens, and the Pt peaks were from the sputtered platinum coating during specimen preparation to reduce charging for SEM analysis.

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Fig. S4 Nitrogen adsorption-desorption isotherm of the nanotubular rutile titania material prepared by burning of the as-prepared titania/cellulose composite sheet (deposition of titania thin films was repeated 20 times).



Fig. S5 Electron micrographs of the nanotubular rutile titania obtained by flame burning of the as-prepared titania/cellulose composite sheet. (a, b) Deposition of titania thin films was repeated 10 times, (a) FE-SEM overview image of the material, (b) SAED pattern of the sample. (c, d) Deposition of titania thin films was repeated 5 times, (c) FE-SEM overview image of the material, (d) SAED pattern of the sample.



Fig. S6 Electron micrographs of the nanotubular rutile titania material obtained by calcination of the asprepared titania/cellulose composite sheet at 1000 °C for 2 h. Deposition of titania thin films was repeated 20 times. (a) FE-SEM image of the material, the inset is a photograph of the material. (b) TEM image of an individual rutile titania nanotube, the inset is the SAED pattern of the sample.



Fig. S7 (a) XRD pattern, (b) FT-IR spectrum, (c) Raman spectrum, (d) UV–vis spectrum of the nanotubular rutile titania material fabricated by flame burning of the as-prepared titania/cellulose composite sheet. Deposition of titania thin films was repeated 5 times.



Fig. S8 (a) XRD pattern, (b) FT-IR spectrum, (c) Raman spectrum, (d) UV–vis spectrum of the nanotubular rutile titania material fabricated by flame burning of the as-prepared titania/cellulose composite sheet. Deposition of titania thin films was repeated 10 times.



Fig. S9 UV–vis absorption spectra taken during the photolysis of an aqueous solution of methylene blue catalyzed by the nanotubular rutile titania material prepared by burning of the as-prepared titania/cellulose composite sheet (deposition of titania thin films was repeated 20 times).