

Electronic supplementary information

Hierarchical fibrous titanium metal derived from cellulose substance

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Materials and Methods

Anatase titania replicas of ordinary laboratory cellulose filter paper were prepared by means of the approach we reported previously (J. Huang and T. Kunitake, *J. Am. Chem. Soc.*, 2003, **125**, 11834–11835). Ultrathin titania gel films were deposited by a surface sol–gel process using titanium *n*-butoxide (99%, Sigma-Aldrich) as precursor to coat each cellulose nanofibre of the filter paper, and the as-prepared titania/cellulose composite sheets were thereafter subjected to calcination treatment in air at 723 K for 6 hours (heating rate 1 K/min) to remove the cellulose component, leaving pure nanotubular structured anatase titania matter possessing the hierarchical structures and morphologies of the initial filter paper from macroscopic all the way down to nanometre scales. The deposition of titania gel films was repeated for 20 times, and the wall thickness of the resulting anatase titania tubes was about 10 nm.

Calciothermic reduction of the anatase titania replicas of filter paper was carried out in a home-made stainless steel autoclave. The anatase titania matter and calcium chloride (anhydrous, 99.99+%, Sigma-Aldrich) were mixed by grinding, the mixture and calcium granules (99.5%, Sigma-Aldrich) were then placed separately in two steel boats fixed at the opposite sides inside the autoclave chamber. The molar ratio of the anatase titania, calcium and calcium chloride was 2:10:1. The autoclave was thereafter filled with argon gas and sealed, and was placed into a tube furnace. It was heated at 1273 K for 6 hours (heating rate 10 K/min) with argon gas protection. The powders obtained was taken out and was immersed in 1.0 M hydrochloride aqueous solution for 2 hours at room temperature to remove calcium oxide and calcium chloride, after washing with pure water, the microfibrinous titanium metal

was obtained as deep grey powders. As a control study, calciothermic reduction of commercial anatase titania powder (98%, Acros Organics) was carried out by the same process.

To prepare the specimens for electron microscopic observations, the metallic titanium obtained was suspended in ethanol by ultrasonication until homogeneous suspension was obtained, which was dropped onto silicon wafer for FE-SEM observation, or onto carbon coated copper mesh for TEM observation, and the specimens were dried in air. FE-SEM micrographs were obtained on a FEI SIRION-100 instrument working at an acceleration voltage of 25.0 kV, TEM and HR-TEM micrographs were acquired on a FEI Tecnai F20 transmission electron microscope operated at an acceleration voltage of 200 kV. XRD measurements were conducted using a Philips X'Pert Pro diffractometer with a Cu-K α ($\lambda = 0.15418$ nm) radiation source. XPS spectra were measured on a VG Escalab Mark II spectrophotometer equipped with an Mg K α X-ray source at energy of 1253.6 eV, high resolution scans in the titanium regions were operated at 0.2 eV increments with a sweep time of 1000 ms/eV and 30 energy sweeps for each region. The XPS spectra was calibrated according to the C 1s peak at 284.7 eV. As a comparison, XRD and XPS analysis of commercial titanium foil (thickness 0.127 mm, 99.7%, Sigma-Aldrich) were performed. Prior to the spectroscopic measurements, the titanium foil was ultrasonicated for 30 minutes in sodium hydroxide aqueous solution (1.0 wt.%), washed with pure water afterwards, and dried with argon flow.

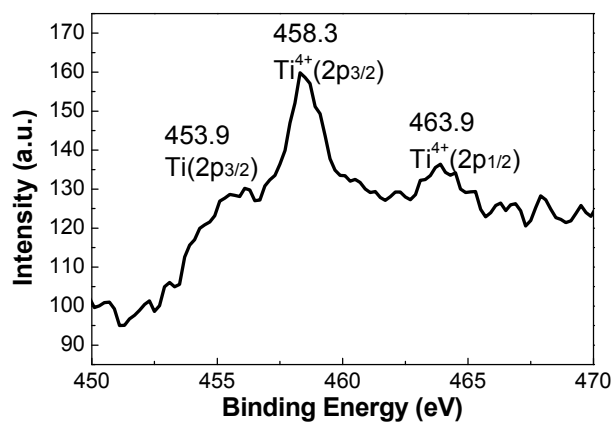


Fig. S1. XPS spectrum of the titanium metal prepared by calciothermic reduction of anatase titania replicas of commercial filter paper at 1273 K without using calcium chloride. The 5.6 eV peak separation between 463.9 eV and 458.3 eV corresponds to that of four-valent titanium ion.

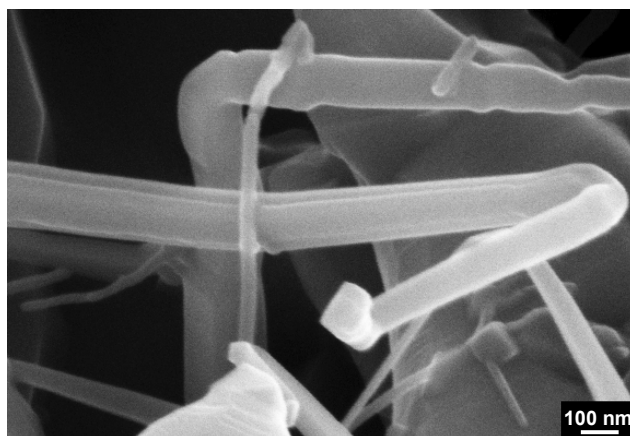


Fig. S2. FE-SEM image of the cross-section part of titanium nanofibres.

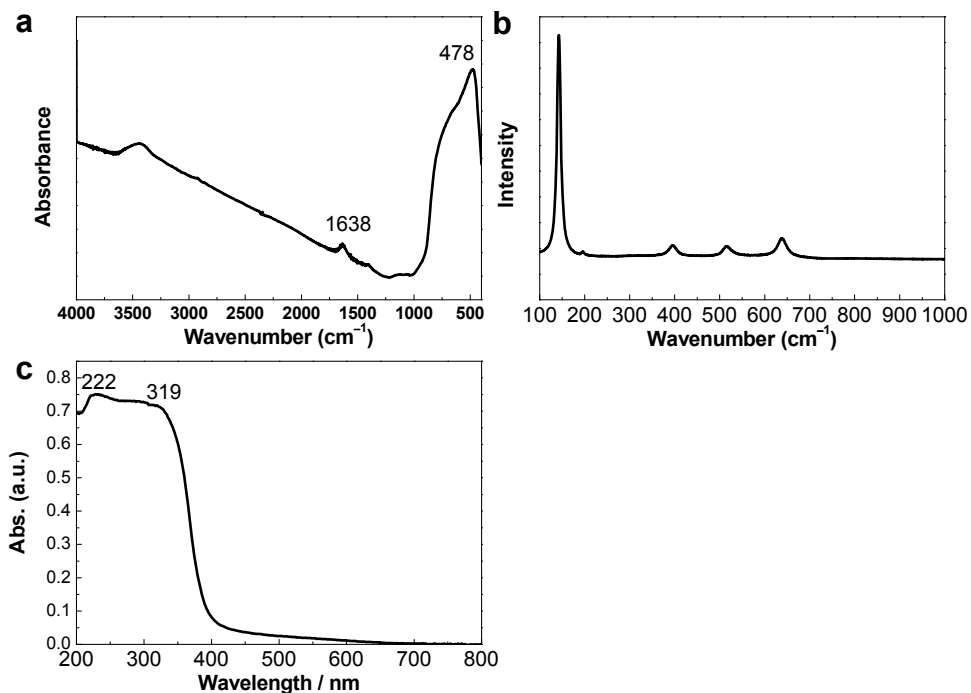


Fig. S3. (a) FT-IR spectrum, (b) Raman spectrum, and (c) UV-vis spectrum of the anatase titania replica of filter paper.

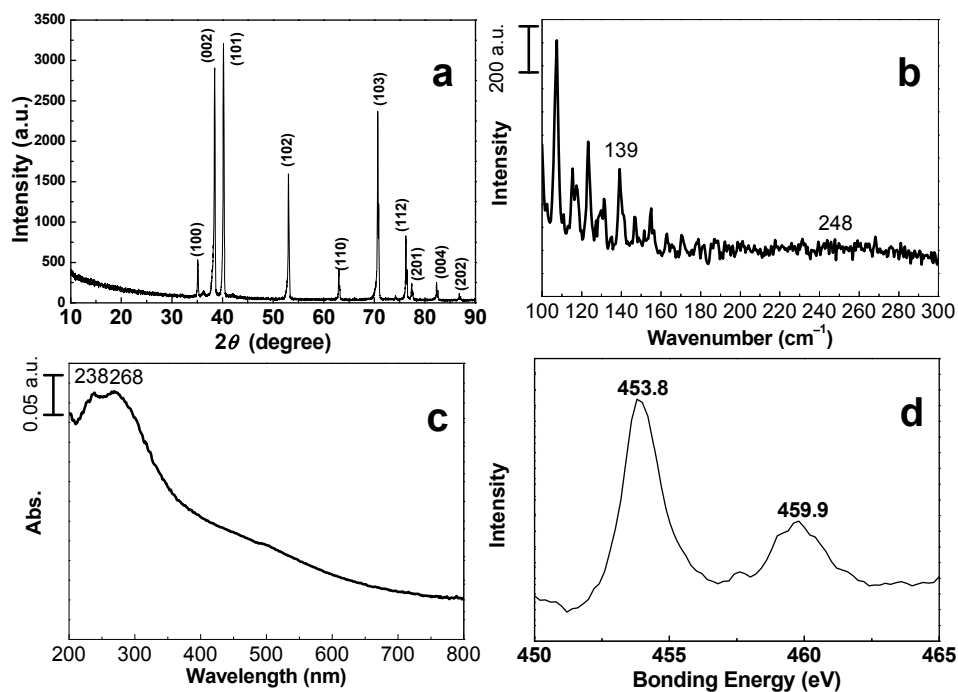


Fig. S4. (a) XRD pattern, (b) Raman spectrum, (c) UV-vis spectrum, and (d) XPS spectrum of commercial titanium foil.

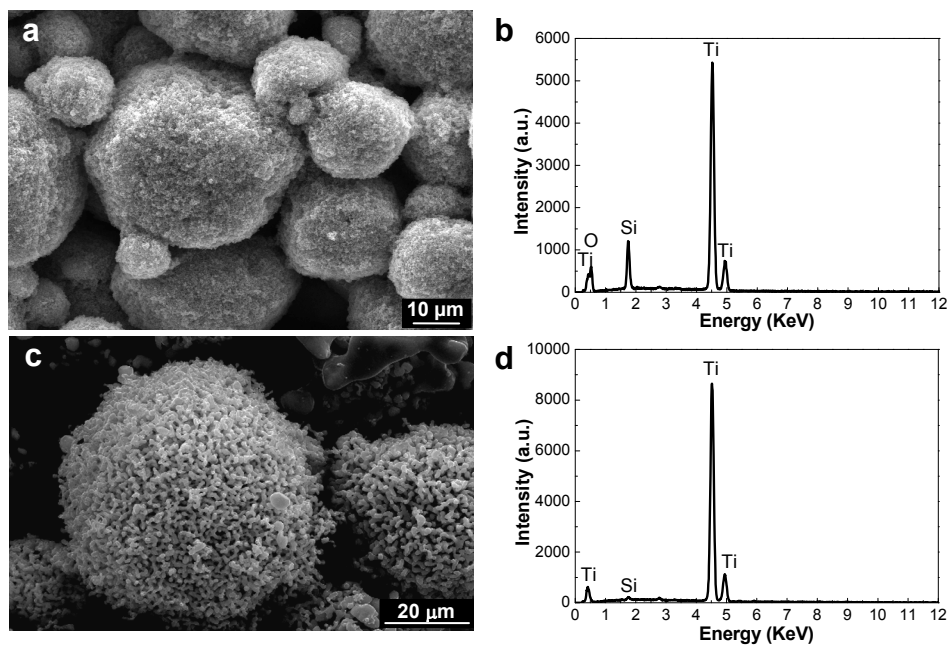


Fig. S5. (a) FE-SEM micrograph and (b) EDX spectrum of the commercial titania powder; (c) FE-SEM micrograph and (d) EDX spectrum of the metallic titanium obtained by calciothermic reduction of commercial anatase titania powder. The Si signal originates from the silicon wafer substrate used to support the specimen for the measurement.