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Supplementary information for:

A general precursor strategy for one-dimensional titania with surface nanoprotrusion and tunable structural hierarchy

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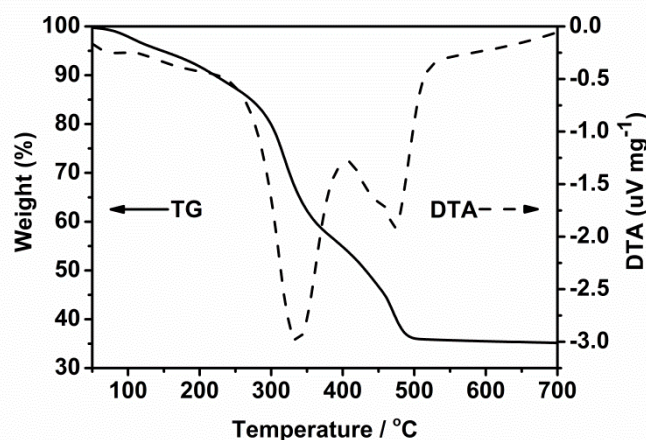


Fig. S1 TG/DTA curves of thermal decomposition of as-electrospun TiO₂/PVP composite nanofibres at a heating rate of 5 °C/min under air atmosphere.

There appear three distinct weight loss stages from room temperature to 700 °C. The first weight loss stage (about 20 %) at < 300 °C is due to the evaporation of adsorbed water and solvent molecules. The second weight loss stage (about 18 %) occurs from 300 °C to 350 °C, and indicates the fast decomposition of PVP in the fibres. During this stage, the DTA curve depicts an endothermic peak at ~340 °C, which indicates the decomposition of TBT along with the degradation of PVP by dehydration in the polymer side chain. It is believed that the PVP on the surface of the fibres decomposed completely first, because the presence of oxygen could give rise to the formation of peroxide residues and decompose easily at relatively low temperature. It is noticed that the PVP inner the fibres is also decomposed partially in this stage. The third weight loss stage (about 27 %) occurs from 350 °C to 500 °C, during which an endothermic peak appears at ~475 °C in the DTA curve, indicating that the TiO₂ phase transforms from anatase to rutile and the residual PVP is decomposed completely. There is no obvious weight loss in the temperature interval from 500 °C to 700 °C, also suggesting the complete decomposition of PVP. Based on the thermal analysis, two calcination temperatures, namely, 350 °C and 450 °C, are selected, and the TiO₂ precursors with controllable crystallinity can be obtained in this study. Besides, calcinating the PVP/TiO₂ fibres at 350 °C for 6 h may be appropriate for the preparation of 1D amorphous TiO₂ precursors, detailed contrast experiments were carried out in the current work.

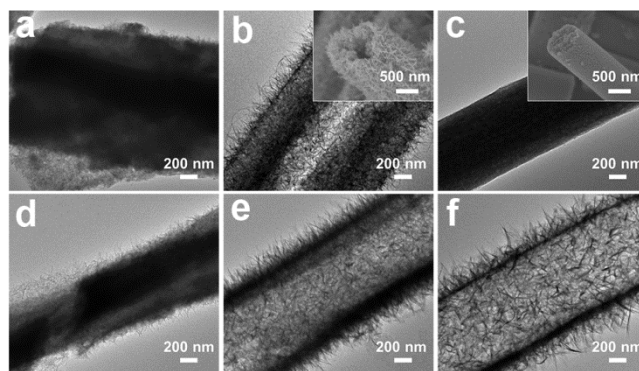


Fig. S2 TEM images of the products obtained after hydrothermal treatment to the precursors calcinated at: (a) 250 °C for 6 h; (b) 300 °C for 6 h; (c) 400 °C for 6 h; (d) 350 °C for 0 h; (e) 350 °C for 2 h; (f) 350 °C for 4 h.

The precursors calcinated at 250 °C for 6 h (a) or 350 °C for 0 h (d) were almost dissolved after the hydrothermal treatment, which was due to the undercomposed PVP under the calcination conditions. When calcinated at 300 °C for 6 h (b and inset), part of PVP inner the PVP/TiO₂ fibres was undercomposed, leading the product invaginated partly. When calcinated at 400 °C for 6 h (c and inset), almost no changes happened after the hydrothermal treatment, which was because that anatase couldn't react with 1 M NaOH under current conditions. When calcinated at 350 °C for 2 h (e) and or 4 h (f), the hollow structures occurred, while the walls of the products seemed asymmetrical. Based on the thermal analysis of the PVP/TiO₂ fibres and the contrast experiments, calcinating the PVP/TiO₂ fibres at 350 °C for 6 h is appropriate for the preparation of 1D amorphous TiO₂ precursors, and well-defined hierarchical hollow titanate can be fabricated after the hydrothermal treatment, which is mainly studied in this work.

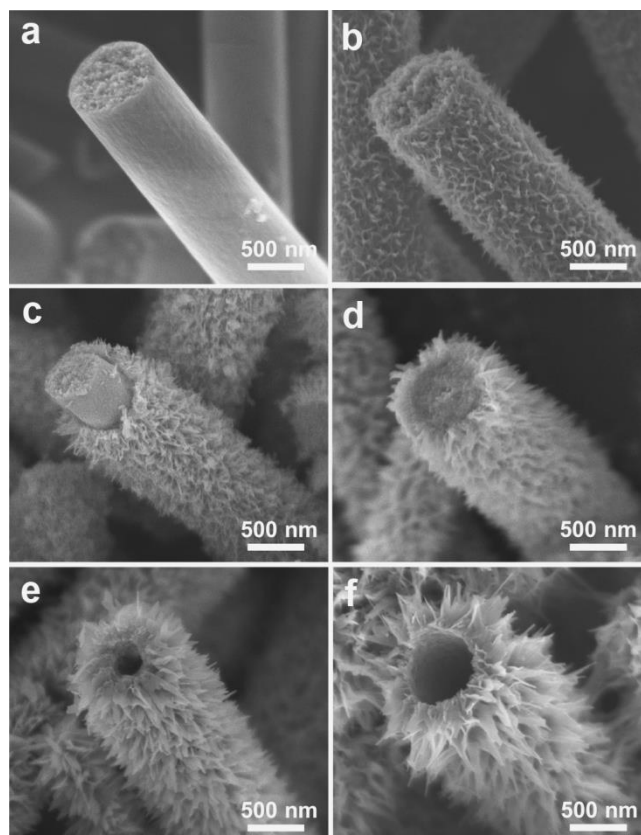


Fig. S3 FESEM images of time-dependent evolution of the 1D-HHT obtained for different hydrothermal time: (a) 0 min; (b) 15 min; (c) 30 min; (d) 1 h; (e) 2 h and (f) 24 h.

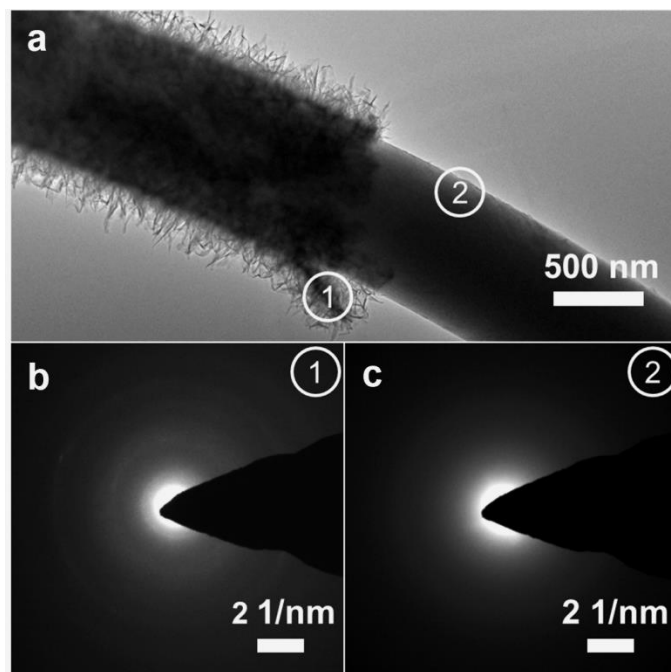


Fig. S4 (a) TEM image of the core-shell fibres obtained by hydrothermal treating at 150 °C for 30 min; (b) SAED pattern of the shell part (①), the several continuous rings indicate that the shell part is crystalline titanate; (c) SAED pattern of the core part (②), the unambiguous first halo ring indicates that the core is still amorphous. The results confirm that the titanate first nucleates *in situ* and grows on the surface of the template fibres. The chemical reaction continues from outside to inside of the amorphous template fibres.

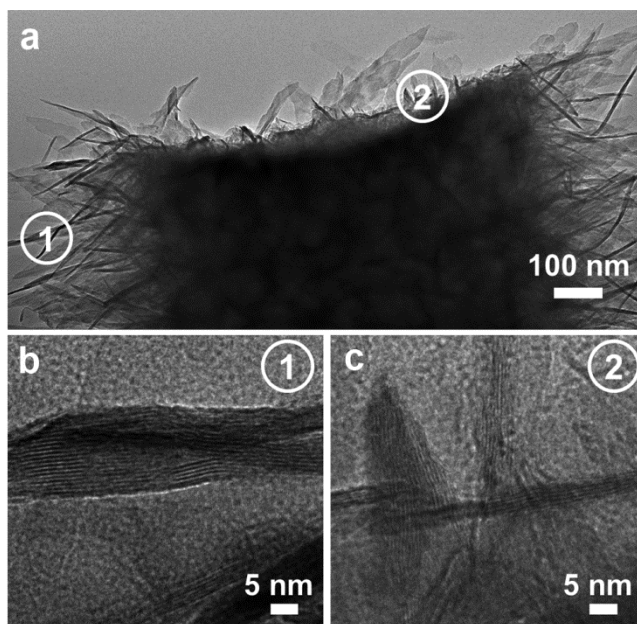


Fig. S5 (a) TEM image of the titanate fibres obtained by hydrothermal treating at 150 °C for 1 h; (b) and (c) HRTEM images of the shell part (①) and the core part (②), respectively. The lattice fringes are clearly observed in the HRTEM images, indicating both of them are crystalline titanate. Because of the space confinement and the gradient reaction from outside to inside of the fibres, the intermediate shows a gradient of crystal size and crystallization.

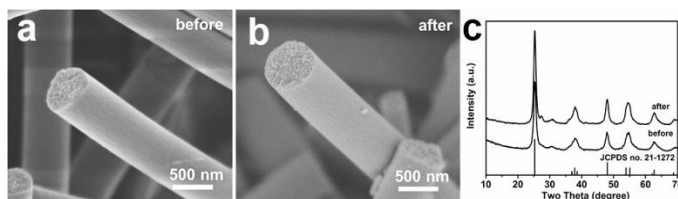


Fig. S6 (a) SEM image of the anatase fibres obtained by calcined at 450 °C for 6 h; (b) SEM image of the sample obtained by hydrothermal treating with 1 M NaOH at 150 °C for 24 h; (c) XRD patterns of the anatase fibres before and after the hydrothermal treating. It is clear that almost no changes happen to the architectures and phase structures after the hydrothermal treating, indicating that anatase can't react with 1 M NaOH under current conditions.

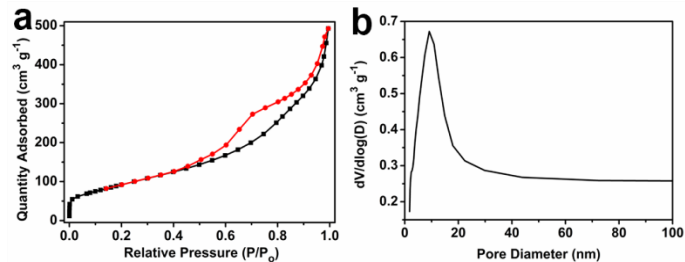


Fig. S7 (a) N_2 adsorption–desorption isotherm of the 1D-HPT; (b) the BJH pore size distribution plot of the 1D-HPT.

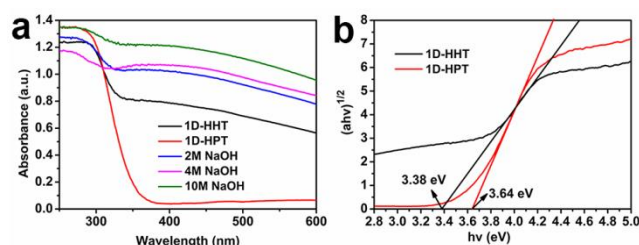


Fig. S8 (a) UV–visible absorption spectra of all the as-fabricated titanates; (b) the plots of transformed Kubelka–Munk function versus the light energy (inset) of the 1D-HHT and 1D-HPT.

Table S1. Textural properties based on nitrogen sorption measurement.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)
P25	54.6
1D-HHT	157.2
1D-HPT	337.0
1D-HHTiO ₂	95.1
1D-HPTiO ₂	104.1