Electronic Supplementary Information (ESI) available for:

A facile strategy to large-scale uniform brookite TiO_2 nanospindles with high thermal stability and superior electrical properties

*Minglei Zhao, Liping Li, Haifeng Lin, Liusai Yang, and Guangshe Li**

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Graduate School of Chinese Academy of Sciences, Fuzhou 350002, P. R. China.

1. Experimental details

1.1 Sample preparation

In a typical synthetic procedure: 22 mmol $TiOSO_4·2H_2O$ was dissolved in 100 mL deionized water and hydrolyzed for 6 h to yield transparent solution. Then, 50 mL of 2.5 M NaOH solution was added with stirring to form a white suspension. This suspension was filtered, washed with deionized water thoroughly, and re-dispersed in 70 mL of 1 M NaOH solution, which the was transferred into a 100 mL Teflon-line stainless steel autoclaves. The autoclave was tightly closed and maintained at 220 ^{o}C for 48 h, and it was allowed to naturally cool down to room temperature. Finally, white precipitates were synthesized, collected, washed with distilled water tens of times, and dried at 60 ^{o}C for 6 h for further characterization.

1.2 Sample characterization

Powder X-ray diffraction (XRD) patterns of the samples were collected using a Rigaku MiniFlex apparatus equipped with Cu Kα radiation (λ=0.15418 nm). Lattice parameters and phase compositions were calculated using a profile fitting by a least-squares method employing the computer program GSAS implemented with EXPGUI.[1] Raman measurements were performed with a Renishaw Raman microscope InVia Plus systems with a ~2λ spatial resolution and 20 mW, 785 nm, semiconductor laser as excitation source. Field-emission scanning microscope (FE-SEM) images of the samples were taken by a JEOL JSM-6700 operated at 10.0 kV beam energy. Transmission electron microscopy (TEM) was performed using a JEOL JEM-2010 with an acceleration instrument of 200 kV. X-ray photoelectron spectroscopy (XPS) was recorded on an ESCA-LAB MKII apparatus with a monochromatic Al Kα X-ray source. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker ELEXSYS E300 spectrometer at liquid nitrogen temperature. The spectrometer was operated in the X-band frequencies with a modulation frequency at 100 kHz. FT-IR spectra of the samples were performed on a Perkin-Elmer Spectrum One spectrometer in the range 400–4000 cm^{-1} with the resolution of 4 cm^{-1} using a KBr pellet technique.

1.3 Electrical measurements

Electrical conductivities of the samples were measured by alternative current impedance technique. The powder samples were pressed uni-axially into pellets with about 7 mm in diameter and 2 mm in thickness. Silver paste was painted onto both sides of the pellets as electrodes. To obtain excellent contact between silver electrodes and pellet, the painted pellets were dried at 200 ^{o}C for 2 h before the test. Alternative current impedance spectroscopy was performed using impedance analyzer (Agilent 4294A) in the frequency range from 40 Hz to 5 MHz for a temperature range from 200 to 500 ^{o}C with an oscillation voltage of 500 mV. All measurements were carried out in air. The impedance data were analyzed by an equivalent circuit model using the software of Zsimpwin (PerkinElmer Instruments).

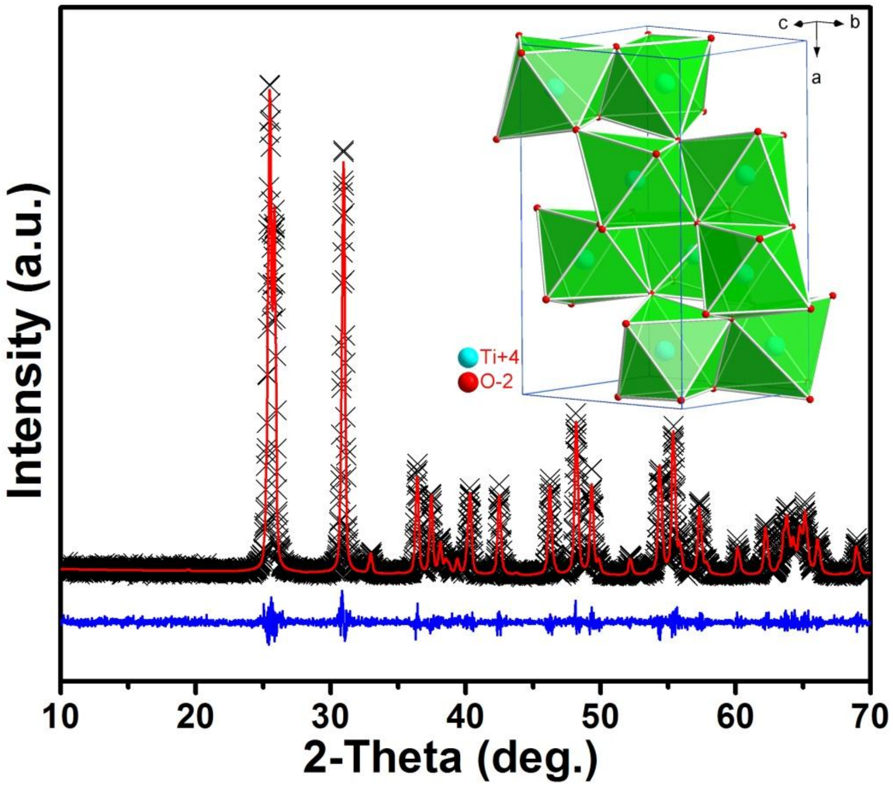

Fig. S1 Rietveld fitting result on powder X-ray diffraction data of the as-prepared TiO_2 sample (R_{wp}=0.1670, R_p=0.1115, R_{-blnk}=0.0944, and χ^2=1.125). The black crosses represent the oberved pattern, the red line corresponds to the calculated diffraction pattern and the blue line is the difference pattern. Inset shows the crystal structure of brookite TiO_2. The calculated parameters using the above Rietveld fitting are a=9.182(1) Å, b=5.4557(9) Å, c=5.1446(9) Å, which are in accordance with the standard data of the brookite TiO_2 (JCPDS no. 29-1360).

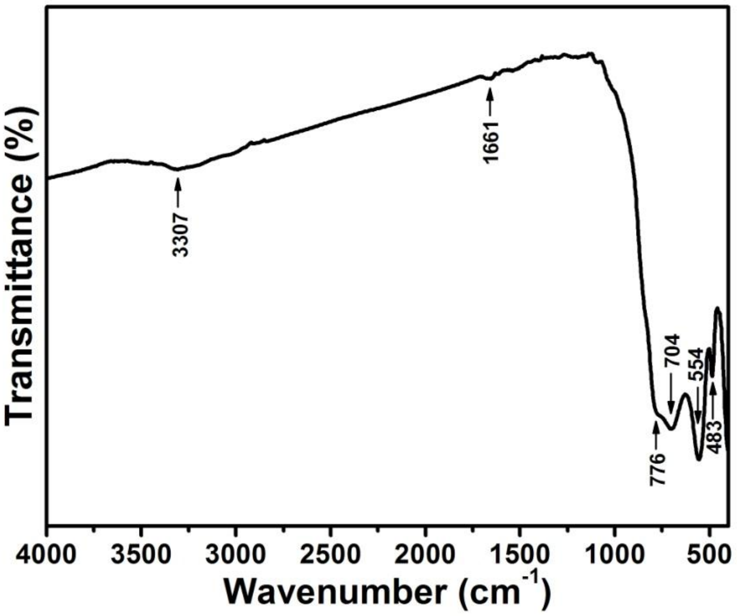

Fig. S2 FT-IR spectra of the as-prepared brookite TiO_2 nanospindles. Four distinct vibrations are observed at 776, 704, 554, and 483 cm^{-1}, characteristic of the bending and stretching vibrations of Ti-O and O-Ti-O bonds in TiO_6 octahedron.[2] The vibrations related with the O-H at 3307 and 1661 cm^{-1} are very weak comparing to other crystals.[3] It is indicated that the brookite TiO_2 nanospindles have clean surfaces.

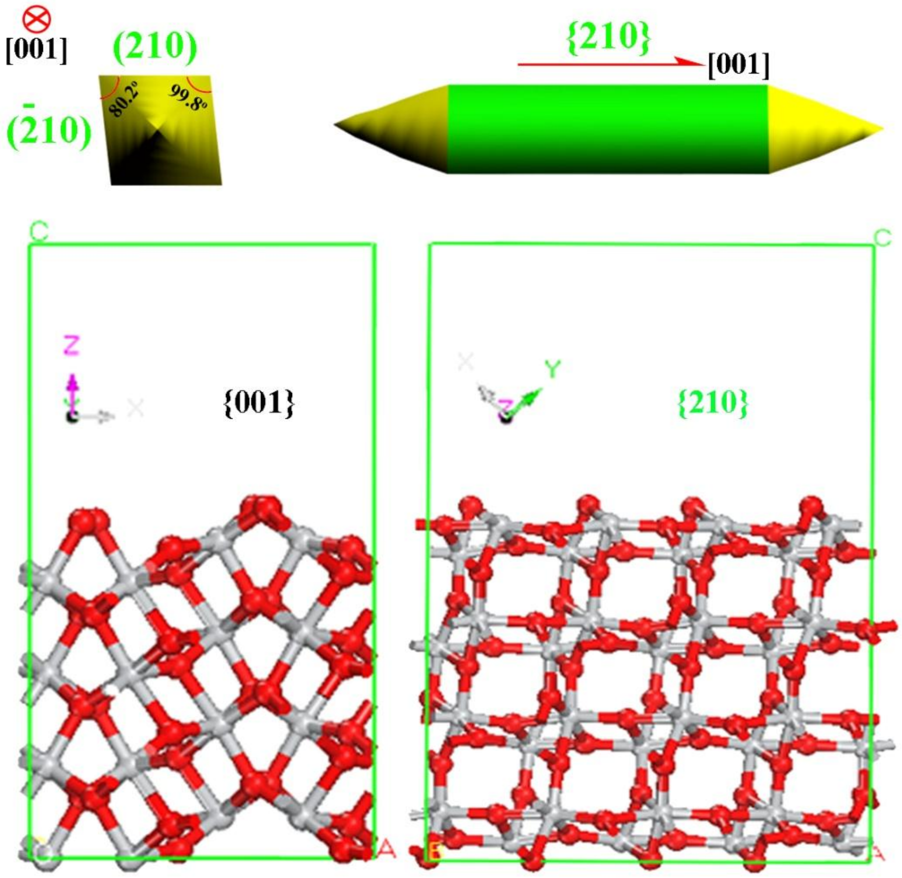

Fig. S3 Surface structures of the brookite TiO_2 nanospindles: {001} (left) and {210} (right) planes. The balls in grey and red represent titanium and oxygen atoms, respectively. The top also depicts the exposed facets in the brookite TiO_2 nanospindles. The exposed atoms in {001} plane are mainly oxygen atoms while plane {210} consists of tatanium and oxygen atoms.

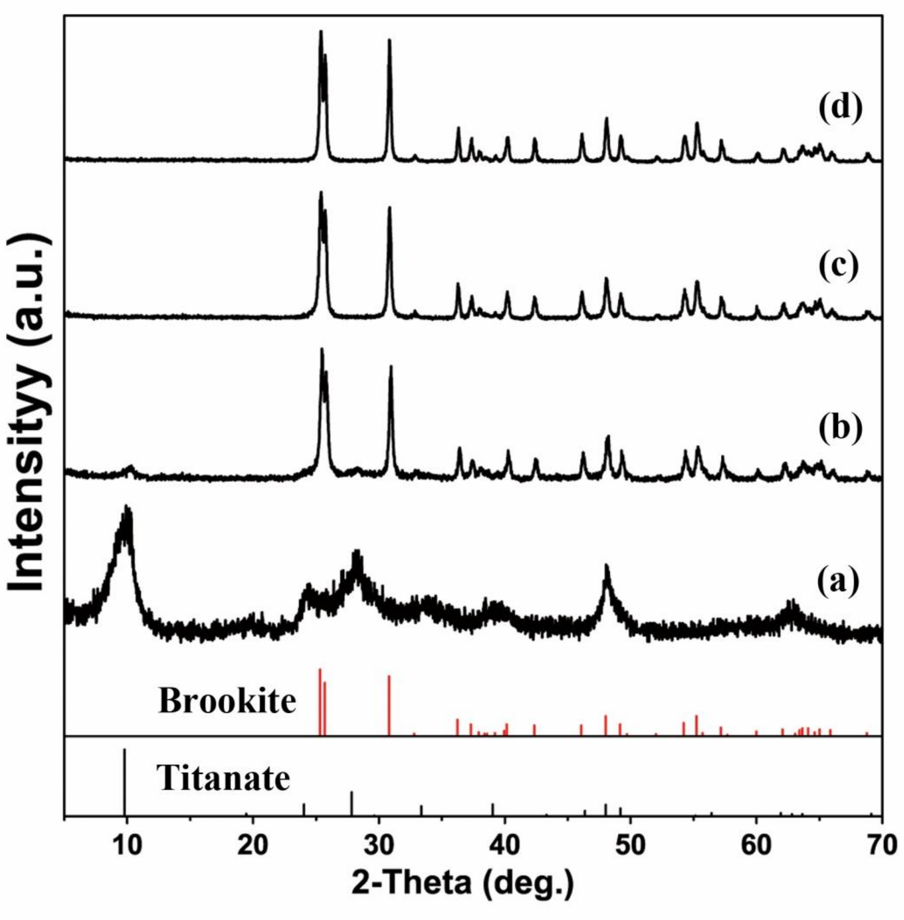

Fig. S4. XRD patterns of comparing samples which were obtained after the reaction for (a) 2 h, (b) 3 h, (c) 6 h, and (d) 12 h. When the reaction time was as short as 2 h, the product is layered titanate (Fig. S4a). After reaction for 3 h, the product was a mixture phase of titanate and brookite (Fig. S4b). Prolonging the reaction time to 6 and 12 h (Fig. S4c-S4d), pure-phase was formed.

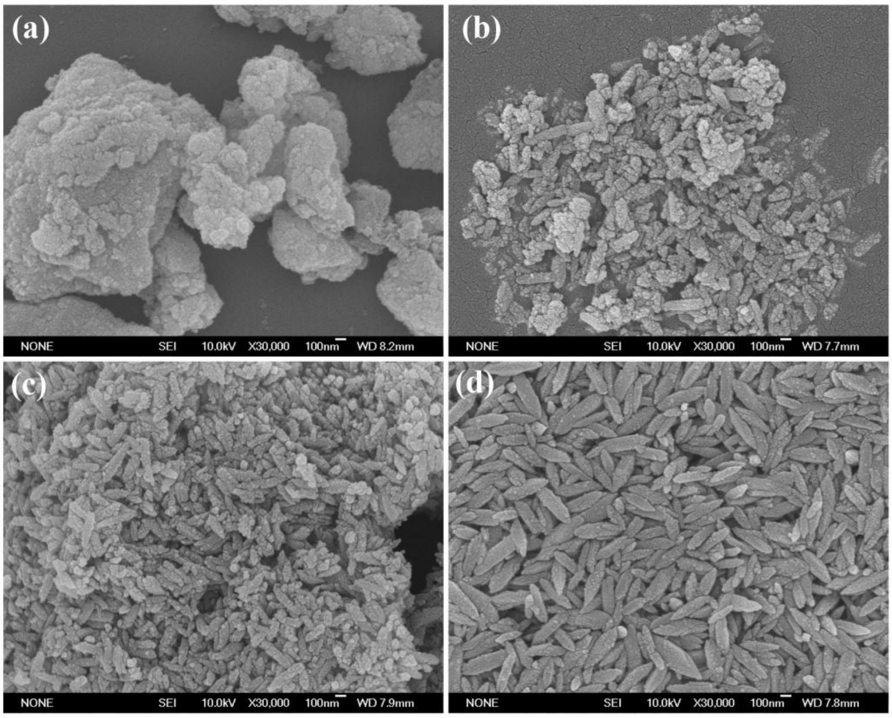

Fig. S5 SEM images of comparing samples which were obtained after the reaction for (a) 2 h, (b) 3 h, (c) 6 h, and (d) 12 h. All the magnifications and scale bars were kept the same. It is found that the sample was consisted of some big aggregates of small particles when the reaction time was as short as 2 h. After reaction for 3 h, some big aggregates decomposed and meanwhile a small number of spindle-like nanoparticle appeared. Further increasing the reaction time, the numbter of spindle-like nanoparticles was increased and the dispersity of the sample was improved. For instance, the sample was composed of large-scale monodisperse nanospindles when the reaction time increased to 12 h.

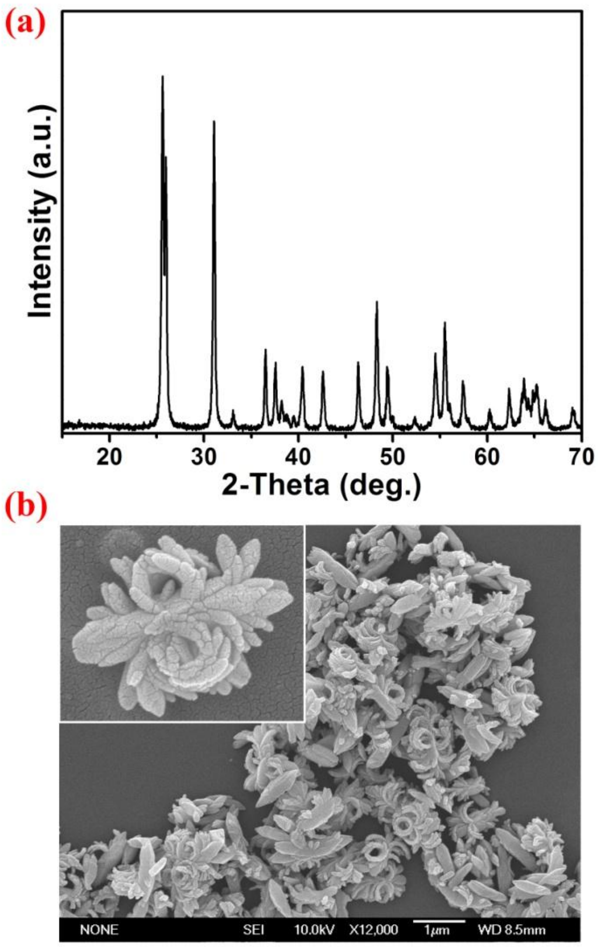

Fig. S6 (a) XRD and (b) SEM image of the sample obtained when the concentration of OH^- species was slightly lowed, and kept other prepared conditions unchanged. All diffraction peaks in Fig. S6a matched well the orthorhombic brookite TiO_2, while no other peaks from other phases or impurities can be detected, which indicates a pure phase. Fig. 6b shows the morphology of the sample obtained at a slightly lower concentration of OH^- species. It can be seen that the sample posssessed flower-like morphology although the pure-phase brookite TiO_2 maintained.

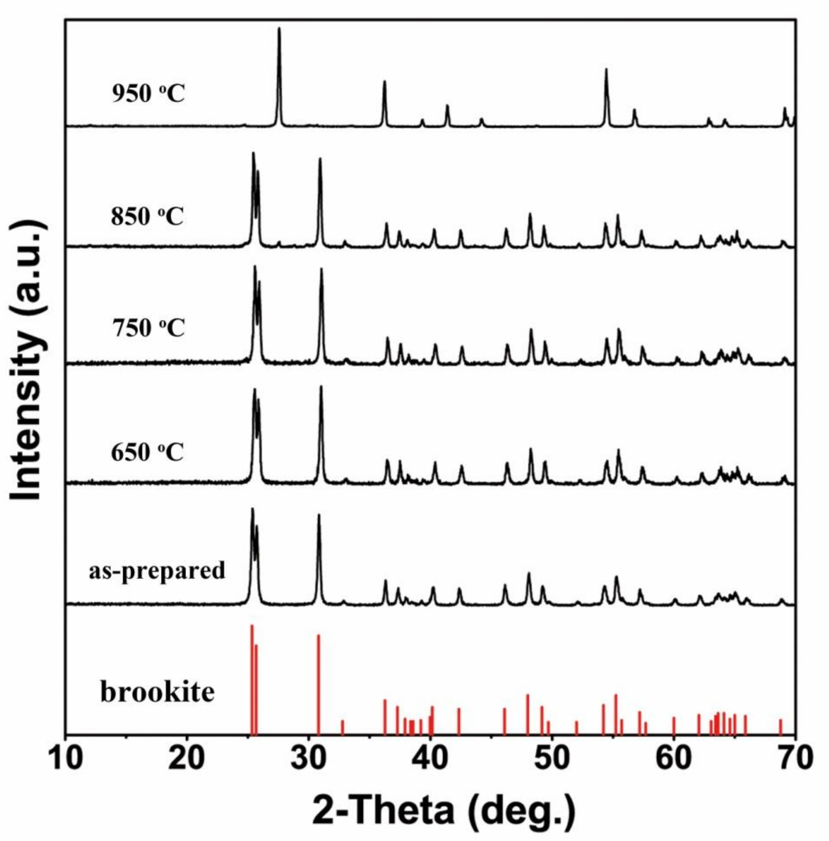

Fig. S7 XRD patterns of the samples obtained by calcined treatment over the spindle-like brookite TiO_2 at given temperatures for 4 h. The obtained monodisperse brookite TiO_2 nanospindles could stabilize at a much higher temperature compared with the literature data.[4] After calcined at 850 ^{o}C for 4 h, only a small fraction (2 wt%) of rutile phase was detected. The temperature that these brookite TiO_2 nanospindles completely transformed into rutile must be as high as 950 ^{o}C.

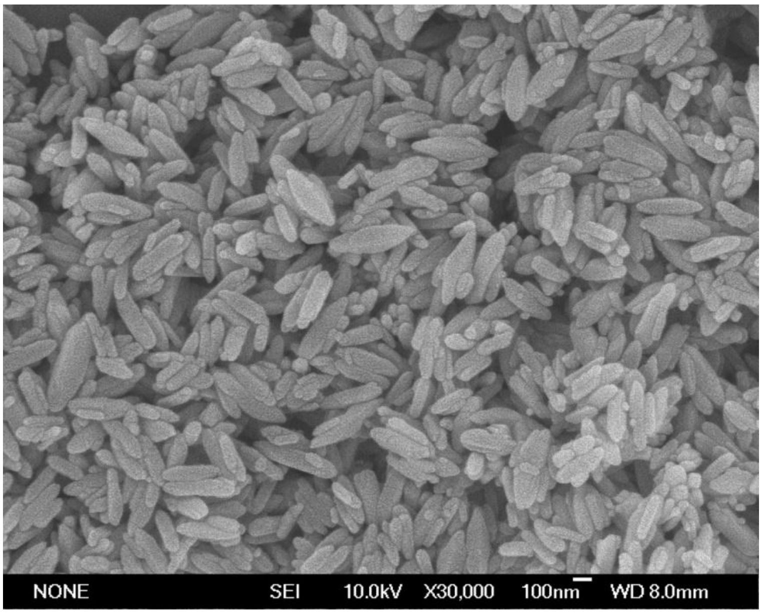

Fig. S8 SEM image of the nanospindles after annealing at 650 ^{o}C for 4 h.

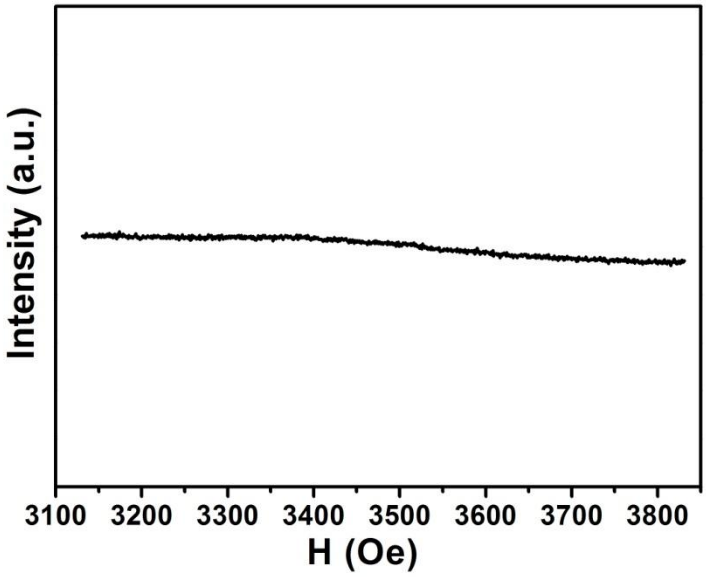

Fig. S9 EPR spectrum of the monodisperse brookite TiO_2 nanospindles. The EPR spectrum of the as-prepared brookite TiO_2 was characterized by a flat baseline without any paramagnetic signal, which indicates the absence of Ti^{3+} species.[5]

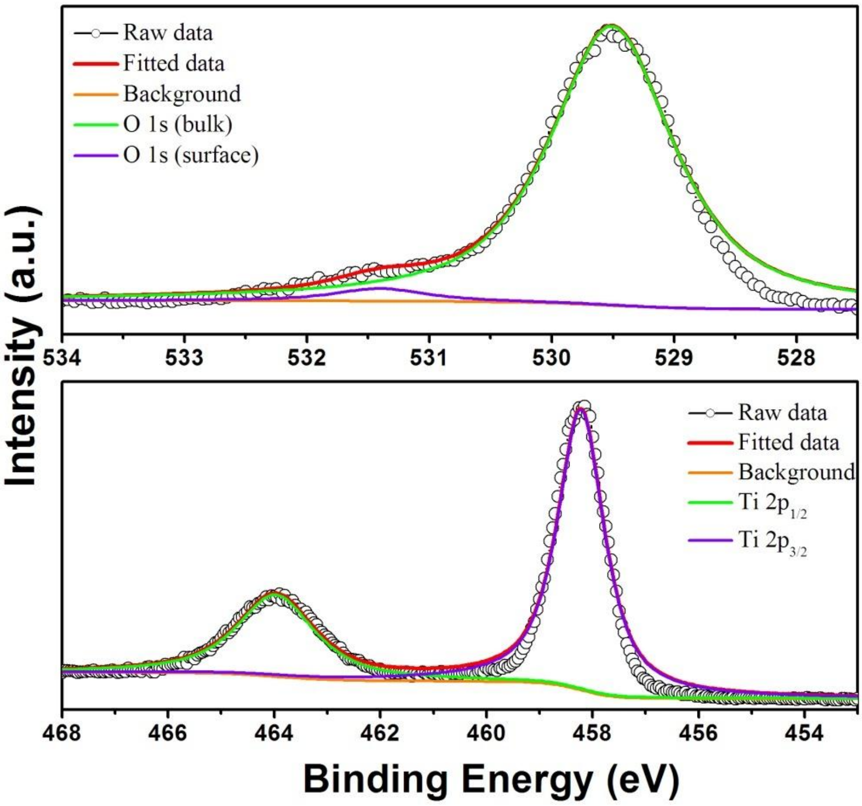

Fig. S10 XPS spectra of the uniform brookite TiO_2 nanospindles.

The valence states of Ti ions of the as-prepared uniform brookite TiO_2 nanospindles were determined by XPS. As illustrated in Fig. S9, the O 1s spectrum consists of a strong photoelectron signal around 529.8 eV and a shoulder around 531.5 eV, which are attributed to the bulk oxygen (O^{2-}) and surface adsorbed oxygen, respectively. Ti 2p spectra consist of the distinct Ti $2p_{1/2}$ and Ti $2p_{3/2}$ photoelectron signals that are located at 464.3 and 458.5 eV, respectively. The spin-orbital splitting between these peaks is 5.8 eV, which is comparable with that of 5.74 eV reported previously.[6] Both Ti 2p signals are highly symmetric, and no shoulders were observed on the lower energy sides of Ti $2p_{3/2}$ signal. Moreover, the bonding energy difference, ΔE, between O1s and Ti $2p_{3/2}$ is 71.3 eV, which is close to that of 71.5 eV for TiO_2, but is smaller than that of 73.4 eV for Ti_2O_3 and 75.0 eV for TiO, indicating the extremely low defect concentration from Ti^{3+}.[7]

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