

Electronic Supplementary Information for

A facile solution-based approach to photocatalytic active branched one-dimensional TiO₂ array

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Experimental procedure

Fabrications of the branched one-dimensional TiO₂ array

Surface cleaned Ti plate $5 \times 5 \times 0.01$ (cm³) in size was immersed in 50 ml 8.8 M H₂O₂ solution containing 16 mM melamine (C₃H₆N₆) and 0.290 M HNO₃, which was kept in an oven maintained at 80 °C for 48 h. The Ti plate covered with the nanowire array was rinsed gently in distilled water and dried at 80 °C. In a typical synthesis, the titanate nanowire array was firstly subjected to an intermediate thermal treatment in air at 260 °C for 1 h, which introduced TiO₂ seeds in the nanowires. A final H₂SO₄ treatment was then carried out by immersing the Ti plate covered with the nanowire array in 50 ml 0.01 M aqueous H₂SO₄ solution at 80 °C for 72 h to achieve the branched one-dimensional TiO₂ array. The sample was designated as HS260, where HS denotes the H₂SO₄ treatment and 260 denotes the intermediate calcination temperature.

Thin film characterizations

Surface morphology of thin films was observed using a field emission scanning electron microscopy (FESEM, Hitachi S-4800, Tokyo, Japan). The X-ray diffraction (XRD) measurements were performed using a Rigaku D/max-3B diffractometer (Tokyo, Japan) with Cu K α radiation ($\lambda = 0.154056$ nm), operated at 40 kV, 36 mA. The high-resolution transmission electron microscopy (HRTEM) examination was conducted employing a JEM-2010 microscopy (JEOL, Japan) working at 200 kV. To prepare the samples for TEM characterizations, the branched 1D TiO₂ was detached off from the Ti plate and then placed on a carbon pre-coated copper grid. Raman spectra were collected using an Almega dispersive Raman system (Nicolet) and a Nd:YAG intracavity doubled laser operating at 532 nm with an incident power of 10 mW. The UV-Vis diffuse reflectance spectra were collected using a UV-Vis near-infrared spectrometer (UV-3150, Shimadzu, Japan). The X-ray photoelectron spectroscopy (XPS) spectra were measured using an ESCA spectrometer (S-Probe ESCA SSX-100S, Fisons Instrument) and monochromatized Al K α X-ray (1486.8 eV) irradiation. The binding energy was normalized to the C 1s energy (284.6 eV) for adventitious hydrocarbons as the indirect standard.

Photocatalytic activity evaluations

The photodegradation of 50 mL sulfosalicylic acid (SSA) solution with an initial concentration of 10 mg/L, in the presence of the titania film 2.5 cm \times 2.5 cm in area, was conducted for up to 2 h in a pyrex reactor with a water jacket. For each run, 20 ppm H₂O₂ was added to accelerate the photocatalytic reaction. The irradiation was

provided by a UV lamp. The average intensity of UV irradiance reaching the samples was measured to be ca. 3.5 mW/cm², using a UV irradiance meters (Model: UV-A Beijing Normal University, China, measured for the wavelength range of 320–400 nm with a peak wavelength of 365 nm for UV light). The solution was stirred and exposed to air during the photocatalytic reaction. Before turning on the lamp, the solution was stirred in dark for 120 min to establish the adsorption/desorption equilibrium between SSA and the TiO₂ film. The SSA concentration was monitored with a UV-Vis spectrophotometer (UV-1800PC, Shanghai Mapada, Shanghai, China) at a wavelength of 208 nm, using a quartz cuvette of 1 cm of the optical path length.

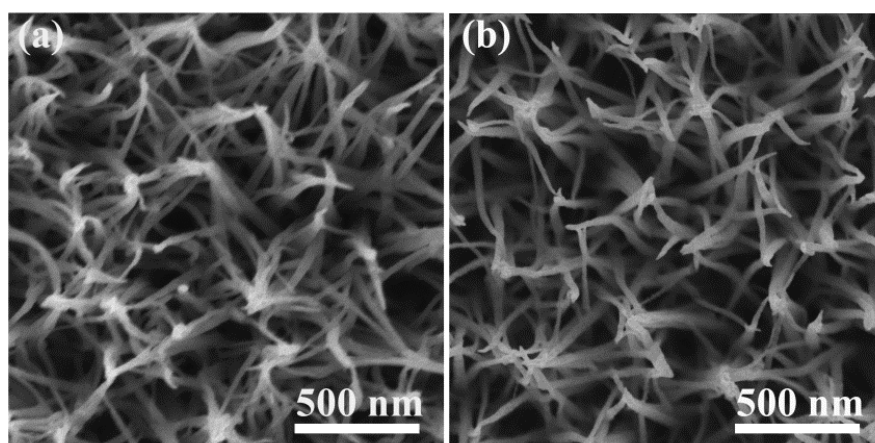


Figure S1 FESEM images of the as-synthesized titania nanowires (a, NW) and that after a subsequent calcination in air at 450 °C for 1 h (b, HT450).

The morphology of nanowires remained unchanged upon the calcination in air at 450 °C for 1 h.

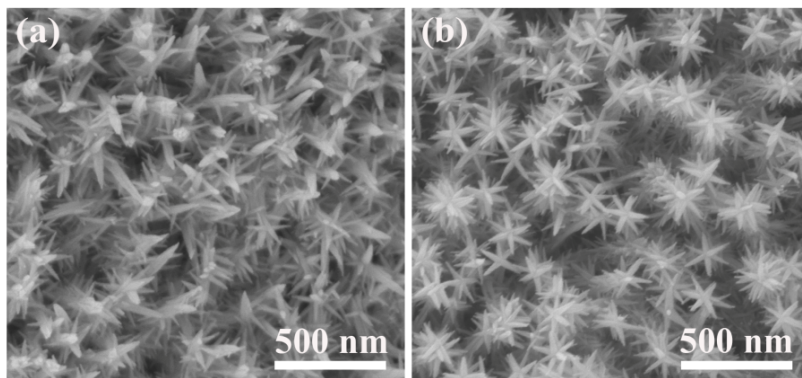


Figure S2 FESEM images of titanate nanowires after the final H_2SO_4 treatment at 80 °C for 72 h, with an intermediate thermal treatment at 240 °C (a) and 250 °C (b).

With the intermediate calcination in air for 1 h at 240 °C and 250 °C, the titanate nanowires changed to branched 1D TiO_2 array upon the final H_2SO_4 treatment at 80 °C for 72 h.

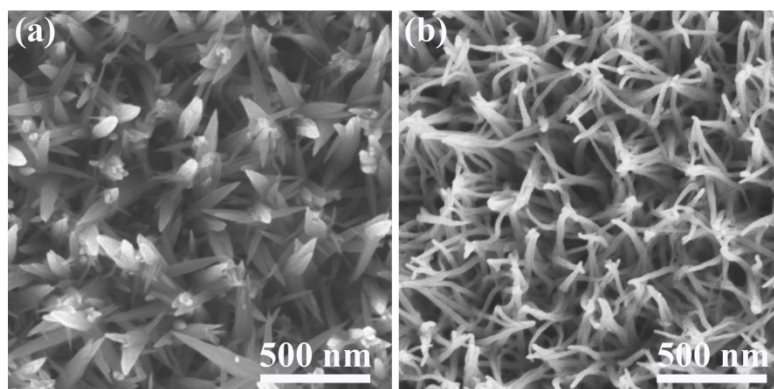


Figure S3 FESEM surface morphologies for thin films of the titanate nanowires after the final H_2SO_4 treatment at 80 °C for 72 h: without (a, HS) and with an intermediate thermal treatment at 300 °C (b, HS300).

Without the intermediate calcination, the titanate nanowires changed to 3D TiO_2 nanoflowers upon the final H_2SO_4 treatment at 80 °C for 72 h. The H_2SO_4 treatment induced no remarkable change in the morphology when the titanate nanowires were previously calcinated at temperatures beyond 300 °C.

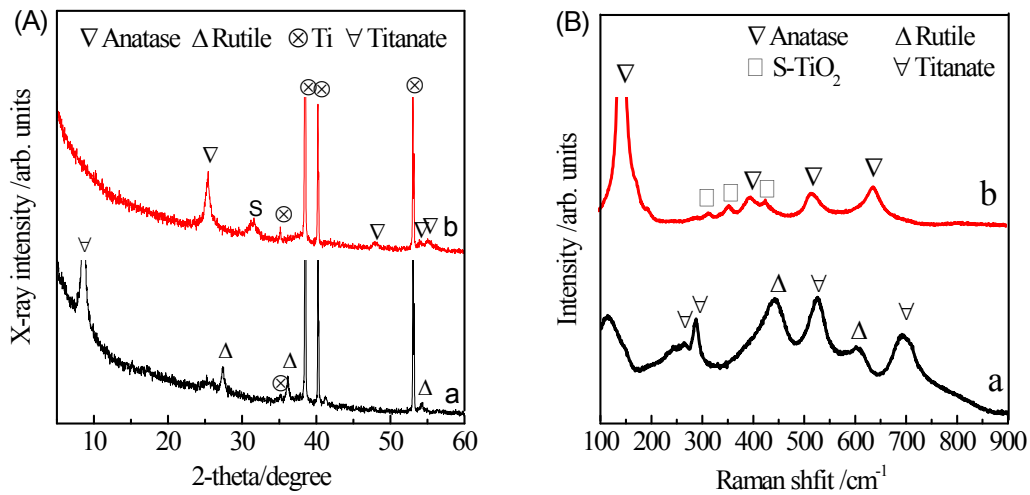


Figure S4 XRD patterns (A) and Raman spectra (B) for thin films of the titanate nanowires after the final H_2SO_4 treatment at $80\text{ }^\circ\text{C}$ for 72 h: without (a, HS) and with an intermediate thermal treatment at $300\text{ }^\circ\text{C}$ (b, HS300).

Without the intermediate calcination, the titanate nanowires partly changed to rutile TiO_2 nanoflowers upon the final H_2SO_4 treatment at $80\text{ }^\circ\text{C}$ for 72 h. When the titanate nanowires were previously calcinated at temperatures beyond $300\text{ }^\circ\text{C}$, the phase composition (anatase plus trace srilankite) remained unchanged upon the final H_2SO_4 treatment (comparing Fig. S4b with Fig. S5 that follows).

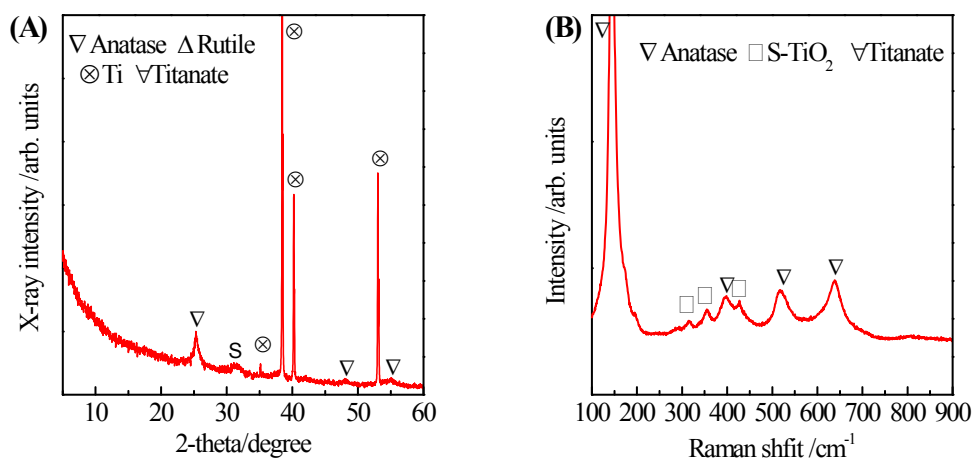


Figure S5 XRD patterns (A) and Raman spectra (B) for the titanate nanowire array after a subsequent calcination at 300 °C (HT300).

The nanowires calcinated at 300 °C consisted of anatase, with trace srilankite TiO₂.

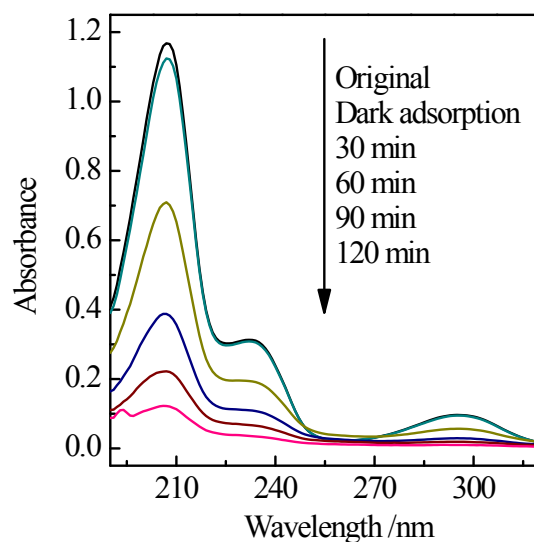


Figure S6 UV-Vis adsorption spectra of SSA in the presence of HS260 and under the UV light illumination for various durations.