

Electronic Supplementary Information for

A facile solution route to deposit TiO₂ nanowire arrays on arbitrary substrates

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Experimental procedure

Material synthesis

Surface cleaning of Ti plates ($5 \times 5 \times 0.01 \text{ cm}^3$) was conducted by etching in a 1:3:6 (in volume) mixture of a 55 mass% HF aqueous solution, a 63 mass% HNO₃ aqueous solution, and distilled water for 1 min, followed by cleaning with water in an ultrasonic bath. The glass substrates ($2.5 \times 2.5 \times 0.1 \text{ cm}^3$) were degreased and cleaned sequentially by sonicating in ethanol and distilled water for 30 min, and were finally dried in air.

Preparation of the precursor solution: Each cleaned Ti plate was immersed in a mixed solution consisting of 50 ml 30 mass% H₂O₂ solution, 100 mg melamine and 1.0 ml concentrated nitric acid, and kept for 48 h in an oven maintained at 80 °C. The Ti plate was then discarded and the remained solution was collected and utilized as the precursor to deposit nanowire arrays on various substrates. The inductively coupled plasma (ICP) atomic emission spectroscopy analysis (IRIS Intrepid II XSP, Thermostat, Massachusetts, U.S.) gave that the precursor contained ca. 0.3 mM hydrated Ti(IV) ions and 0.46 M nitrate ions. The H₂O₂ concentration was ca. 3.2 M, determined by titration using a standard potassium permanganate solution. The metallic Ti plate can be replaced with much cheaper sponge Ti particles instead.

Precipitation of nanowire arrays on glass substrates: A TiO₂ seed layer was deposited on glass substrates by a sol-gel dip-coating method [refer to J. B. Zhong, J. Z. Li, F. M. Feng, S. Huang, and J. Zeng, *Mater. Lett.*, 2013, **100**, 195.]. Glass substrates were dipped in a titania sol and then withdrawn at a speed of 36 cm/min under a relative humidity of ca. 20%, followed by calcination in air at 450 °C for 1 h. The substrates covered with the seed layer were immersed in 15 ml precursor, and maintained at 80 °C for up to 6 h. After the deposition, the substrates were rinsed with water, dried, and subjected to a thermal treatment at temperatures up to 550 °C for 1 h in air. Alternatively, to achieve a low temperature crystallization, the as-synthesized nanowires were immersed into an aqueous HCl solution (12.5 mM, 50 ml) and maintained at 80 °C for 72 h.

Precipitation of nanowire arrays on other substrates: The precipitation of nanowire arrays on FTO, ITO, silicon wafer, stainless steel mesh and glass rod was the same to the above-mentioned route on glass substrates. For the glass fibers, the seed layer was prepared by immersing in a 1.5 M TiCl₄ aqueous solution, which was maintained at 60 °C for 3 h, followed by rinsing in distilled water, dried, and calcinated in air at 450 °C for 1 h. For carbon cloth, the TiO₂ seed layer was not necessary. The nanowire array on carbon cloth was achieved by directly immersing carbon cloth without any seed layer in the precursor solution and maintained at 80 °C for 24 h.

Preparation of P25 nanoparticulate film: Particles of a commercial P25 (Degussa, Germany) TiO₂ (an average particle size of 30 nm and BET surface area of 50 m²/g) were deposited on the pickled Ti plates by repetitively dipping them in an ethanolic suspension of 25 g/L and drying in air at 105 °C to achieve an weight increase of 1 mg/cm², which roughly corresponds to a film thickness of 3 μm on each side.

Characterization

The deposited thin films were observed by using a field emission scanning electron microscopy (FESEM, Hitachi S-4800, Tokyo, Japan). Transmission electron microscopy (TEM) observations were conducted with a JEM-2010 microscopy (JEOL, Japan) working at 200 KV. X-ray diffraction (XRD) experiments were performed using an Empyrean diffractometer (PANalytical B.V., Netherlands) with a Cu K α radiation, operated at 40 kV, 40 mA ($\lambda = 0.154056$ nm). The UV-Vis spectra were collected using a SHIMADZU UV-3150

UV-NIR spectrometer.

Photocatalytic activity evaluation

Photocatalytic activity was evaluated by photodegradation of 50 ml rhodamine B aqueous solution with an initial concentration (c_0) of 0.005 mM, in the presence of a titania film with an area of 2.5 cm \times 2.5 cm. The irradiation was provided by a 500 W Xe-lamp that was 16 cm over the solution. The average intensities of UV and visible irradiance reaching the sample were 5.0 and 200 mW/cm², respectively, measured for the wavelength range of 320-400 nm with a peak wavelength of 365 nm for UV light, and 400-1000 nm for visible light (Model: UV-A and FZ-A, Beijing Normal University, China). During the photodegradation reaction, the dye solution was magnetically stirred under the ambient environment. The change in rhodamine B concentration (c) was evaluated by monitoring the maximal absorbance at the wavelength of 553 nm using a UV-Vis spectrophotometer (UV-1800PC, Shanghai Mapada Instruments Co. Ltd, Shanghai, China).

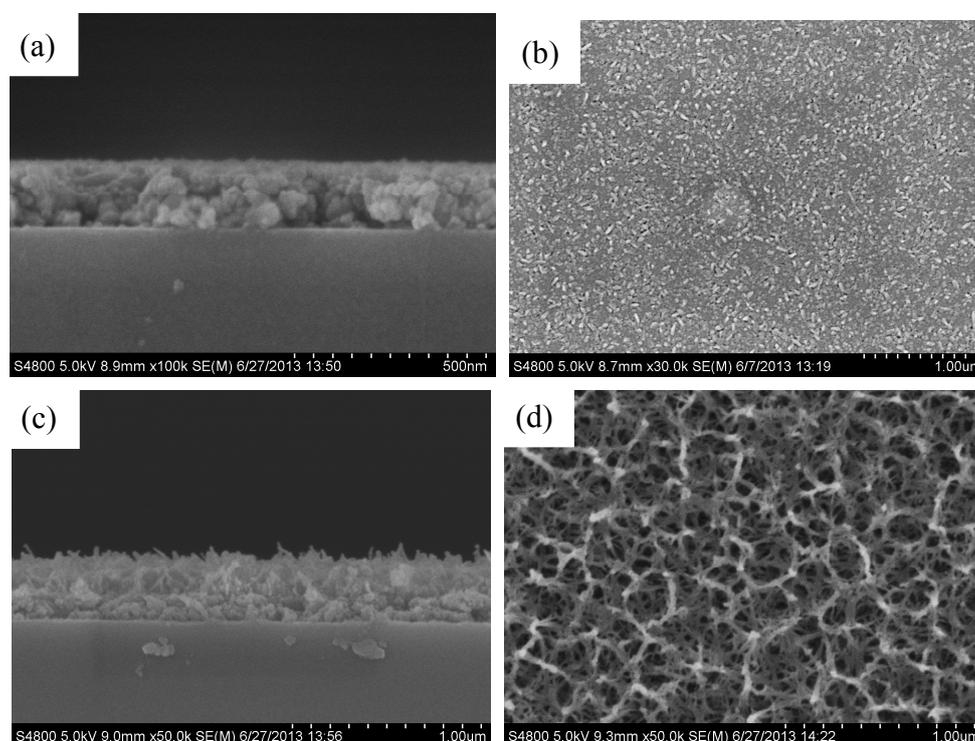


Fig. S1 FESEM images of (a, b) the sol-gel anatase seed layer on glass substrate, and (c, d) nanowires grown at 80 °C for 3 h.

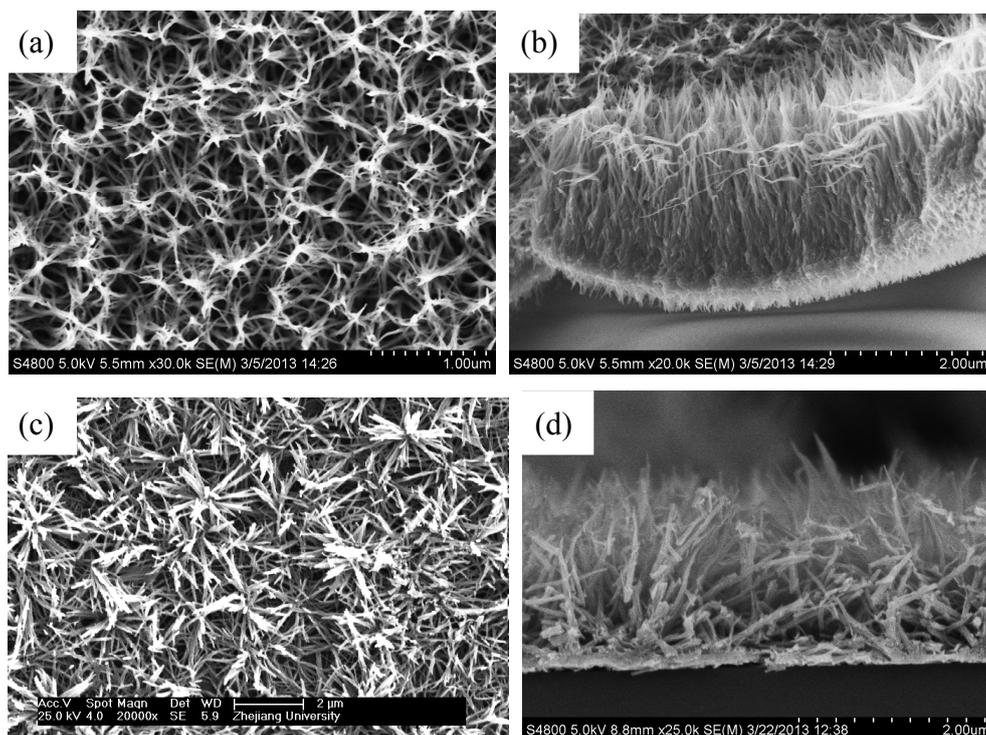


Fig. S2 FESEM images of anatase nanowires on glass substrates grown at 80 °C for 48 h: (a, b) with sol-gel anatase seed layer; (c, d) without seed layer. All the films were subjected to a final calcination in air at 450 °C for 1 h.

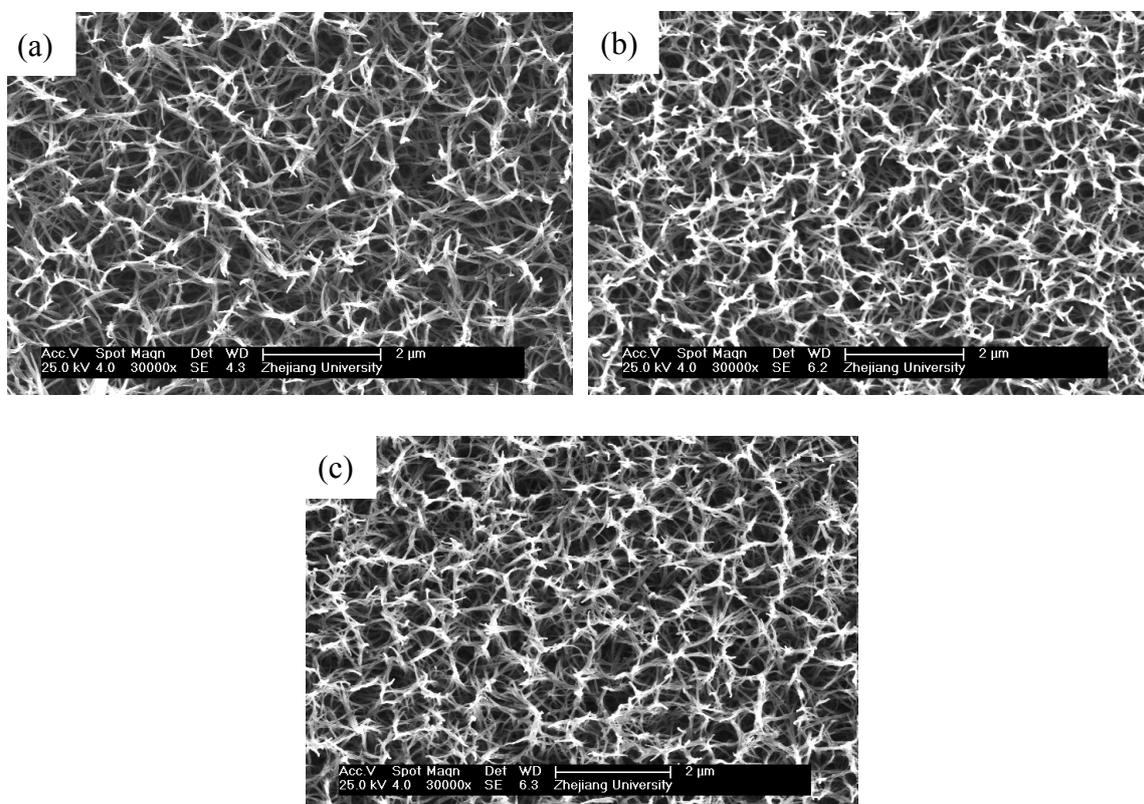


Fig.S3 FESEM images of anatase TiO₂ nanowires on substrates of (a) FTO, (b) ITO, and (c) silicon wafer, grown at 80 °C for 24 h.

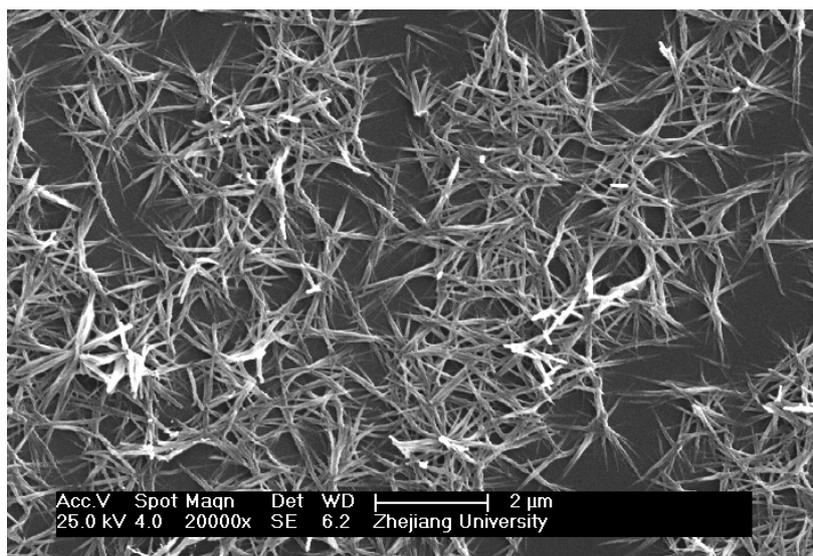


Fig. S4 FESEM images of anatase nanowires on glass substrates without seed layer, grown at 80 °C for 6 h.

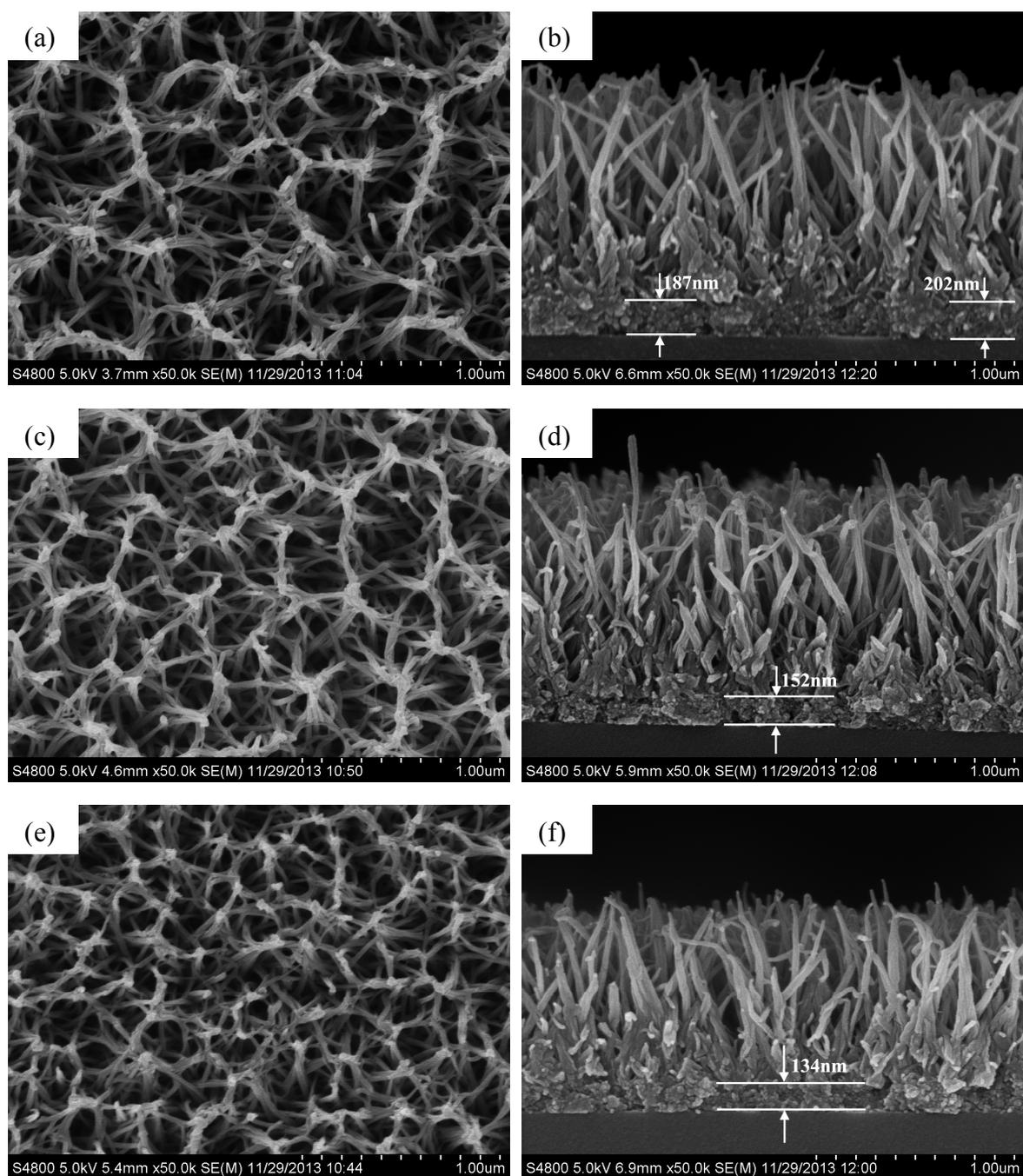


Fig. S5 FESEM images of the as-synthesized nanowires on glass substrates with sol-gel anatase seed layer, grown at 80 °C for 6 h. The sol-gel anatase seed layer was deposited by spin coating at a speed of (a, b) 1200 rpm, (c, d) 5200 rpm, and (e, f) 8200 rpm to achieve different film thickness, followed by a subsequent calcination in air at 450 °C for 1 h.

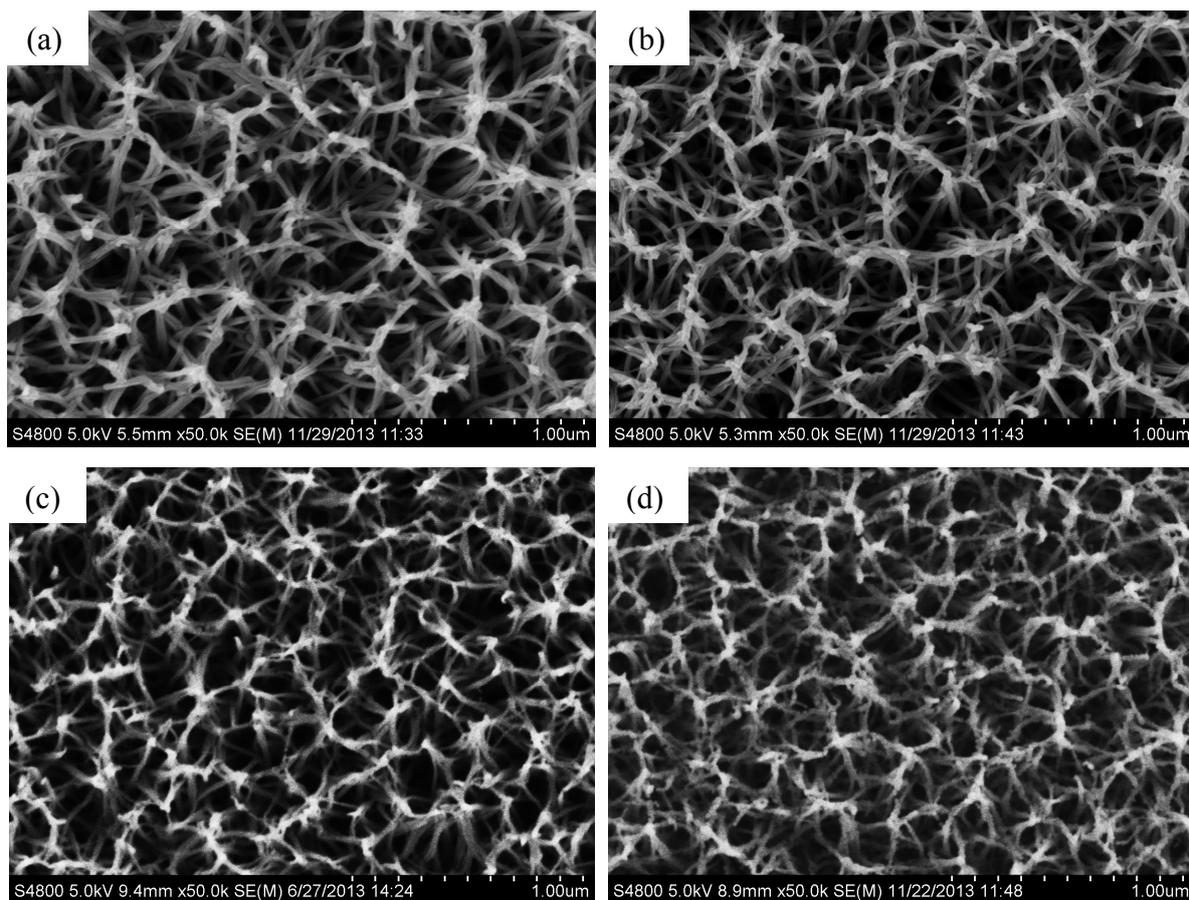


Fig. S6 FESEM images of (a) the as-synthesized nanowires on glass substrates, grown at 80 °C for 6 h, and those followed by calcinations in air for 1 h at (b) 300 °C, (c) 450 °C, and (d) 550 °C.