Supporting information

Orientated thin film of anatase TiO_2 nanocrystal array for self-cleaning coating

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Chemicals and Materials: Tetrabutyl titanate (TBT) (AR grade) and concentrated sulfuric acid (95–98% by weight) were purchased from Beijing Chemical Reagent Company. Rhodamine B (RhB) (AR grade) was purchased from Aladdin Reagent Company. Polyvinylpyrrolidone (PVP M.W.130M) was purchased from Alfa Aesar Reagent Company. All other chemicals were used without further purification.

Preparation of Anatase quasi 1D TiO_2 Nanowires Array (TNWA): In a typical synthesis, FTO substrates ($F:SnO_2$) were washed with acetone, ethanol and mili-Q water and then dried in air. First, a dense TiO_2 buffer layer was coated on clean FTO by spin-coating TiO_2 sol-gel precursor at 2000 rpm for 60 s. The TiO_2 sol–gel precursor was prepared using the modified method previously reported.[1,2] Briefly, 0.68 g of tetrabutyl titanate (TBT) and 0.4 mL concentrated hydrochloric acid (36.5%~38% by weight) were dissolved in 10 mL isopropanol and stirred about 30 min, then filtered through a 0.22 μm syringe filter. The substrates were annealed at 450°C for 60 min at a ramping rate of 3°C/min in a muffle furnace.

To grow the TiO_2 nanowires array, the substrates with dense TiO_2 layer were placed face-down in a Teflon-lined stainless steel autoclave. The hydrothermal precursor solution was prepared by mixing 0.5 g tetrabutyl titanate (TBT) and 1.0 g polyvinylpyrrolidone (PVP) in 30 mL dilute sulphuric acid solution (2.0 mol/L). After the precursor solution was stirred for 30 min, the solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave. Subsequently, the autoclave was sealed, put into electronic oven, and maintained at 180 °C for 6–24 h.

Photocatalytic Activity Measurements: The photocatalytic activity of the samples was evaluated through the decolorization of rhodamine B (RhB) spin coating on the substrates under UV light 150 W high voltage mercury lamp (mercury vapour lamp, the central wavelength of 360 nm) at a 20 cm distance. The experiments were performed at 25 ˚C as follows: rhodamine B (RhB) ethanol solution (0.5g/L) was spin-coated on the substrate at 1000 rpm for 60s. Before measurements, the substrate was exposed under UV light for 30 min to eliminate atmospheric oxidation of RhB. The RhB concentration was monitored by the absorbance value at the maximum peak (520 nm) using a Shimadzu UV-3600 UV–Vis–NIR spectrophotometer. The degradation efficiency (Eff) was evaluated according to Eff (%) = $(1 - I/I_o) \times 100\%$, where I_o and I represent the absorbance of the dye before and after irradiation, respectively.

Characterization: The crystalline structure was recorded by using an X-ray diffractometer (XRD) (Bruker AXS D8 Focus), using Cu Kα radiation (λ= 1.54056 Å). Transmission electron microscope (TEM) images were taken using an FEI Tecnai G2 operated at 200 kV. Scanning electron microscope (SEM) images were measured on a JEOL JSM 4800F. The UV–Vis absorption spectra were recorded on a UV-3600 UV–vis–NIR scanning spectrophotometer (Shimadzu).The contact angle (CA) of water on the surface was measured using a DSA10-MK2 drop shape analysis system (Krusess). The TiO_2 nanocrystals array thin film coated FTO was placed into a DSA 10-MK2. A drop of water was (~ 20 μL) placed on the sample. A picture was taken and analyzed with the contact angle analysis software.

1. J.-Y. Liao, B. X. Lei, Y. F. Wang, J. M. Liu, C. Y. Su, D. B. Kuang, *Chem. Eur. J.* 2011, **17**, 1352–1357.

2. E. Scolan, C. Sanchez, Chem. Mater. 1998, 10, 3217-3223.

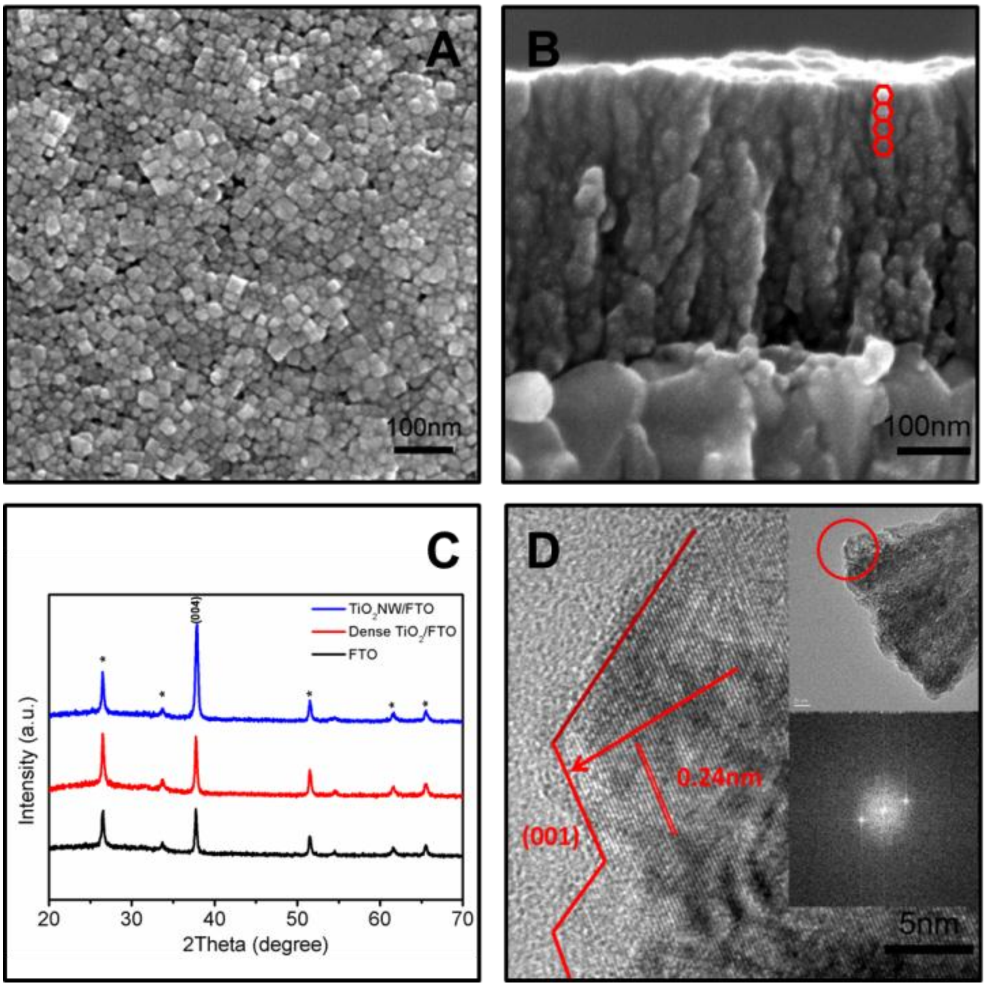

Fig. S1. Electron microscopy and XRD characterizations of anatase TiO_2 nanowires array synthesized from 0.5 g TBT in 30ml of 2.0 mol/L H_2SO_4 at 180 ^oC for 6 hours. (A) Field emission (FE) SEM images (plan view) of anatase TiO_2 nanowires array. (B) FE-SEM cross-sectional images of anatase TiO_2 nanowires array. (C) XRD patterns of FTO glass (black), dense TiO_2 layer (red) and anatase TiO_2 nanowires array (blue) on FTO glass. (D) High-resolution TEM micrographs of anatase TiO_2 nanowire edge. Top inset shows a piece of TiO_2 nanowires array. Bottom inset shows a fast Fourier transform micro-graph from the image area in D.

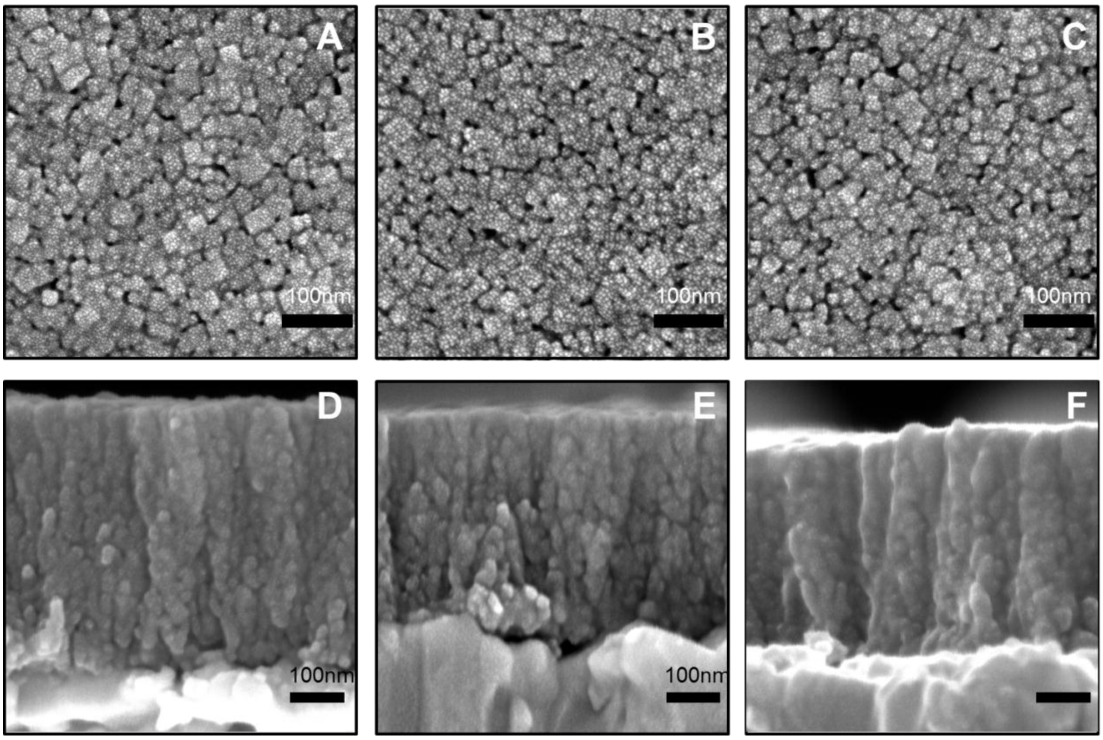

Fig. S2. FE-SEM images (plan and cross-section view) of TiO_2 nanowires array obtained from 0.5 mL TBT and different amount of PVP in 30 mL of 2 mol/L H_2SO_4 solution at 180 ^{o}C for 6 hours. A, D for 0.5 g PVP, B, E for 1.5 g PVP and C, F for 2.0 g PVP.

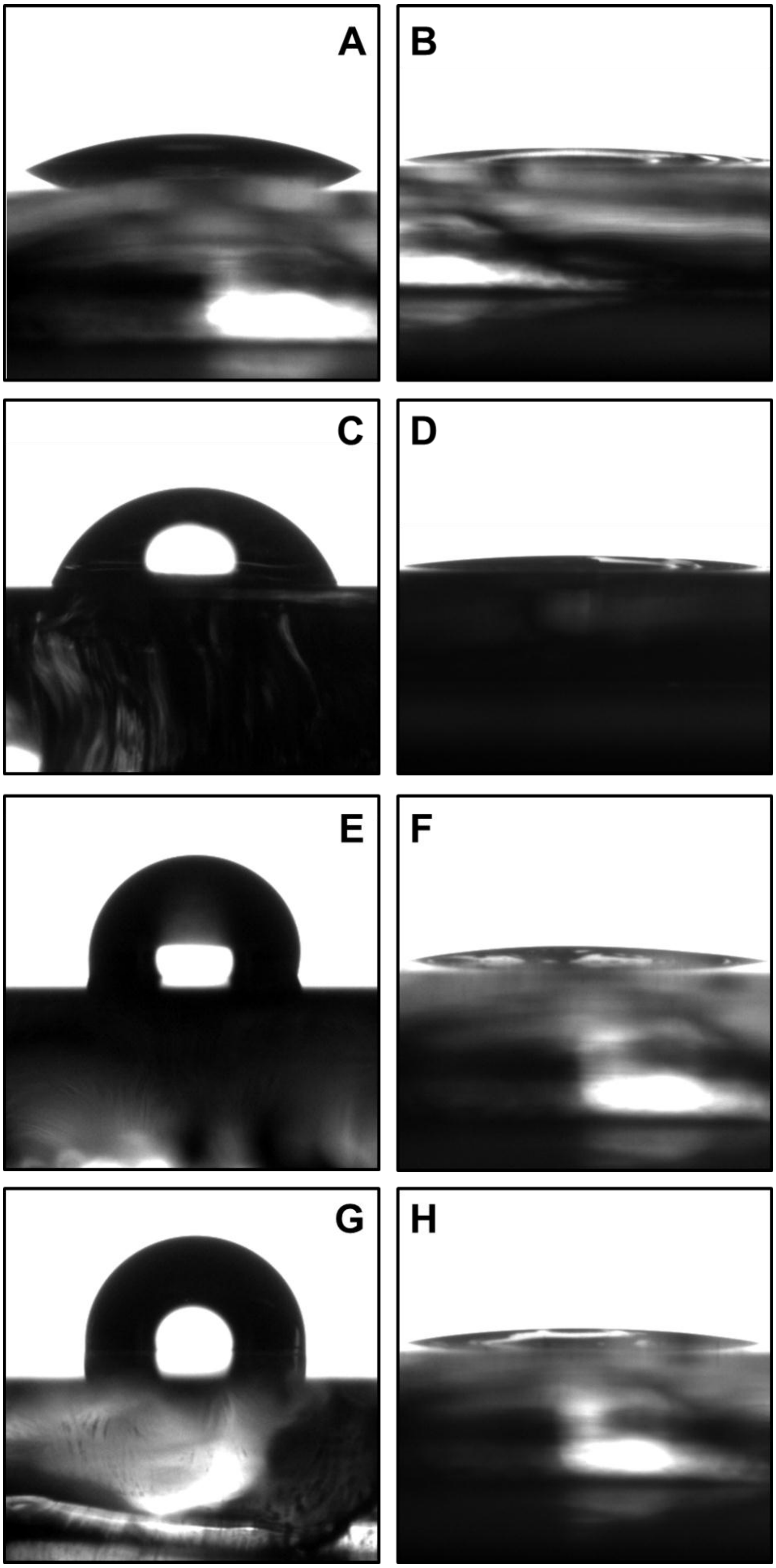

Fig. S3. Optical image of contact angle of TiO_2 nanowire array coating on FTO glass synthesized from 0.5 g TBT and 1.0 g PVP in 30 mL of 2.0 mol/L H_2SO_4 solution at

180 ^{o}C for 6, 12, 24 and 48 hours, left column is before UV treatment, right column is after UV treatment.