Supporting information

Orientated thin film of anatase TiO$_2$ nanocrystal array for self-cleaning coating

Zhao Zhao, a,b Huaqiao Tan, a Haifeng Zhao, a Di Li, a Min Zheng, a Peng Du, a,b Guoqiang Zhang, a,b Dan Qu, a,b Zaicheng Sun, a* and Hongyou Fan, a,c,d

a State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences. 3888 East Nanhu Road, Changchun, Jilin 130033, P. R. China. sunzc@ciomp.ac.cn

b University of Chinese Academy of Sciences, Beijing, P. R. China.

c The University of New Mexico/NSF Center for Micro-Engineered Materials, Department of Chemical and Nuclear Engineering, Albuquerque, New Mexico 87131, USA.

d Sandia National Laboratories, Advanced Materials Lab, 1001 University Blvd. SE, Albuquerque, NewMexico 87106, USA. hfan@sandia.gov

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. 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/I₀) x 100%, where I₀ 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 TiO₂ 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.

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$_2$SO$_4$ at 180 °C 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 TiO₂ nanowires array obtained from 0.5 mL TBT and different amount of PVP in 30 mL of 2 mol/L H₂SO₄ solution at 180 °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$_2$SO$_4$ solution at
180 °C for 6, 12, 24 and 48 hours, left column is before UV treatment, right column is after UV treatment.