Electronic Supplementary Information

Tetragonal faceted-nanorods of anatase TiO_2 with large percentage of active {100} facets and their hierarchical structure

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Experimental

Preparation of alkali titanate precursors

Synthesis of one dimensional (1D) sodium titanate nanotube (Na-TNT): 4 g P25 was put into 80 mL of 10 M NaOH aqueous solution, then transferred into a 100 mL Teflon-lined stainless steel autoclave, and sealed. The autoclave was put into an oven, heated at 140 °C for 24h, and cooled naturally in air, producing white Na-TNT precipitates. These white precipitates were isolated from solution by centrifugation and subsequently washed with deionized water, the step was repeated for several times until the pH of solution reached to 10.5. Then the Na-TNT was isolated by centrifugation at 10000 r/min for 5 minutes.

Synthesis of urchin-liked sodium titanate (Na-UT): Na-UT were prepared by hydrothermal reaction of titanium foil in NaOH solution with little amount of H_2O_2 solution.[1] Typically, 1.0 g titanium foil (Beijing Henglitai Co., Ltd.) was immersed into 76 mL 0.5 M NaOH solution with 4 mL 30% H_2O_2 solution and then placed into a 100 mL Teflon-lined autoclave. The autoclave was heated at 180 °C for 24 h, and then naturally cooled to room temperature, producing slightly yellow precipitates in the solution. After remove the un-reacted titanium foil, the precipitates were isolated from solution by centrifugation and subsequently washed with deioned water, the step was repeated for several times until the pH of solution was about 10.5 and dried at 60 °C in vacuum for 10 h. Then the synthesized Na-UT samples were annealed in a muffle furnace at 500 °C (heated in advance) for different minutes (5, 10 and 20 min), and the prepared Na-UT precursors were labeled as Na-UT-c, where c means annealing time. For example, Na-UT-10 denotes Na-UT calcined at 500 °C for 10 minutes while Na-UT-0 denotes Na-UT without annealing.

Preparation of {100} facets enclosed tetragonal faceted-rods anatase TiO_2

Nanosize structure: 1 g Na-TNT (wet, isolated by centrifugation without drying) were dispersed into 38 mL deionized water with 2 mL 30% H_2O_2 solution, then transferred to a 50 mL Teflon-lined stainless steel autoclave, and sealed. The autoclave was put into an oven, heated at 180 °C for 24 h, and cooled naturally in air, producing white tetragonal faceted-nanorods (TFNRs) precipitates. These white precipitates were isolated from solution by centrifugation and subsequently washed with deionized water, and finally dried at 60 °C in vacuum for 10 h.

Hierarchical structure: 0.1 g Na-UT-c powders were dispersed into 40 mL deionized water solution, then transferred to a 50 mL Teflon-lined stainless steel autoclave, and sealed. The autoclave was put into an oven, heated at 200 °C for 24 h, and then naturally cooled to room temperature, producing white hierarchically structured anatase TiO_2 precipitates. These white precipitates were isolated from solution by centrifugation and subsequently washed with deionized water, and finally dried at 60 °C in vacuum for 10 h.

Materials Characterization

The morphologies and the structures of the samples were observed by scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM). The high-resolution TEM (HRTEM) images were taken on FEI Tecnai F30 operated at 300 kV. X-ray powder diffraction (XRD) were carried out on a Rigaku D/max-2500 diffractometer (CuKα radiation, λ=0.1542, 40 kV, 100 mA).

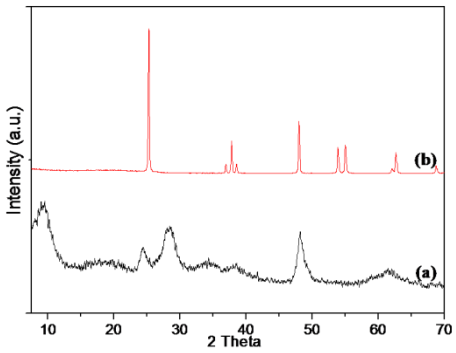

Fig. S1 X-ray diffraction patterns of: (a) Na-TNT precursors and (b) the TFNRs product. The diffraction peaks in Fig. b match well with the crystal structure of the anatase TiO_2 phase (JCPDS 21-1272), indicating that the Na-TNT was completely transferred into an anatase TiO_2 phase.

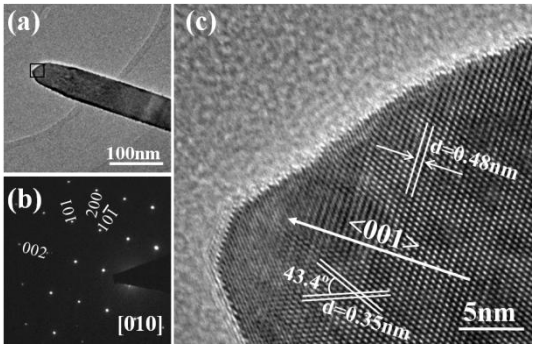

Fig. S2 (a) Typical TEM image of an individual TFNR; (b) the corresponding SAED pattern; and (c) HRTEM image taken from (a) indicated by rectangular, viewing along the [010] direction. Both TEM image and SAED patterns confirm that the TFNR has a single-crystalline structure of anatase TiO_2 (Fig. a, b). Fig. c displays the HRTEM image, three sets of lattice fringes with spaces of 0.35, 0.35 and 0.48 nm can be attributed corresponding to (101), (10-1) and (001) of anatase phase, respectively. The 43.4° angle between (101) and (10-1) is in agreement with the data calculated from the lattice constants of anatase ($I4_1/amd$, a=0.37852 nm, c=0.95139 nm). The axis of the rod was parallel to the <001> direction, indicating that the rod grows along the <001> direction. SEAD patterns confirmed that the faceted-rod was viewed along [010] direction (Fig. b). On the basis of the above observations and structural analysis, we conclude that the exposed lateral facets of the prepared TFNR are mainly the {100} facets. More detailed characterization was shown in our previous report.[2]

References:

1. Y. Mao, M. Kanungo, T. Hemraj-Benny and S. S. Wong, *J. Phys. Chem. B*, 2006, **110**, 702.

2. J. Li and D. Xu, *Chem. Commun.*, 2010, **46**, 2301.