Supporting Information

Synthesis of Anatase TiO_2 Nanocrystal with Exposed {001} Facets

Yunqian Dai[1,2], Claire M. Cobley[1], Jie Zeng[1], Yueming Sun[2] and Younan Xia[1*]

[1]*Department of Biomedical Engineering, Washington University, St. Louis, Missouri 63130*

[2]*School of Chemistry and Chemical Engineering, Southeast University, Nanjing, Jiangsu 211189, P. R. China*

*To whom correspondence should be addressed. E-mail: xia@biomed.wustl.edu

Experimental Section

Electrospinning. The TiO_2 nanofibers were typically prepraed by electrospinning a solution containing 1.5 mL titanium tetraisopropoxide (Sigma, 99.999%), 1.0 mL acetic acid (glacial, Fisher Scientific), 0.15 g poly(vinyl pyrrolidone) (PVP) ($M_w \approx 1.3\times10^6$, Sigma) and 2.5 mL ethanol. The solution was ultrasonicated for at least half an hour to ensure the homogeneity followed by loading into a 3 ml plastic syringe with a 21 gauge stainless steel needle at the tip. The needle was electrified by a high-voltage DC supply (ES30P-5W, Gamma High Voltage Research Inc., Ormond Beach, FL) and a voltage of 15 kV was applied. The solution was pumped continuously by a syringe pump (KDS-200, Stoelting, Wood Dale, IL) with a rate of 0.3 mL/h. A grounded aluminum foil was used as electrode to collect the nonwoven mat of nanofibers. The electrospinning process was conducted in air below the humidity of 35%. The as-spun nanofibers were left in air for ~5 h to let the hydrolysis reaction go to completion. The nonwoven mats of nanofibers were then easily peeled off from the surface of collector using tweezers.

Acid digestion of TiO_2 nanofibers. Acetic acid was used to adjust the pH of Millipore water (18 MΩ, Millipore water) to 1.6 (or other pH values as indicated in the text). 4.0 mg

of the nonwoven mats of TiO_2 nanofibers were added into the above solution. With the assistance of vortexing, the fibers disappeared quickly. The solution was colorless and transparent and then was heated at 80 ^oC with vigorous stirring for 18 h to ensure homogeneity without any observable color changes. The acidic acid was also replaced by various inorganic acids to examine the effect of different anions on the morphology.

Hydrothermal treatment. In a typical procedure, 20.7 mL of the above solution was added to a Teflon-lined autoclave and heated at 150 ^oC for 20 h in an oven. After the reaction was completed, the solution had been separated into two layers - a transparent liquid layer on top which was carefully decanted, and a white precipitate on the bottom (the as-synthesized TiO_2 nanocrystals). The precipitate was thoroughly washed with deionized water at least six times to remove PVP and excess acetic acid.

Characterization. The washed TiO_2 samples were dispersed in deionized water and dropped onto carbon-coated copper grids (Formvar/Carbon, 200 mesh, Ted Pella) for electron microscopy analysis. TEM images were collected using a Tecnai G2 Spirit Twin (FEI) operated at 80 kV. High-resolution TEM was performed using a JEOL JEM-2100F operated at 200 kV. The SEM samples were prepared by dropping the washed samples onto a silicon wafer and letting them dry in air, followed by gold sputter-coating (except for the nonwoven mats sample which was not coated). SEM images were taken using a Nova NanoSEM 230 field-emission scanning electron microscope (SEM, FEI, Hillsboro, OR) operated at an accelerating voltage of 10 kV. The crystal structure information was obtained with X-ray diffraction (Rigaku Geigerflex D-MAX/A Diffractometer using Cu-Ka radiation).

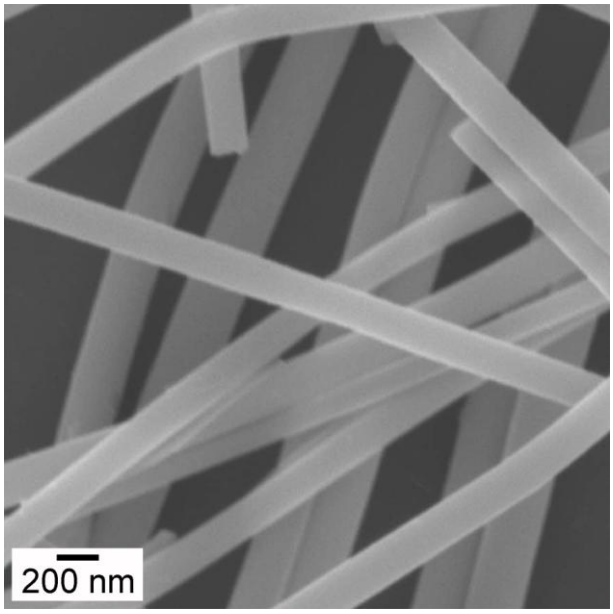

Figure S1. SEM image of a nonwoven mat of composite nanofibers consisting of amorphous TiO_2 and poly(vinyl pyrrolidone) (PVP).

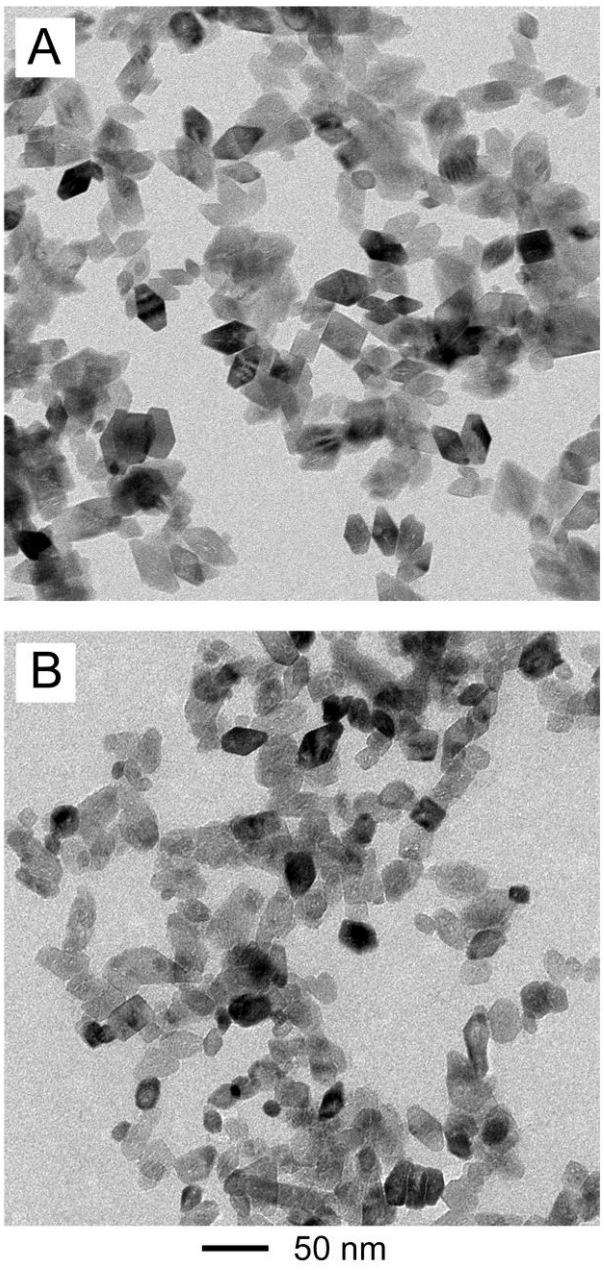

Figure S2. Effect of electrospinning on the morphology of resultant TiO_2 nanocrystals. TEM images of TiO_2 nanocrystals synthesized by (A) using an electrospinning process, (B) directly injecting an identical solution into an acetic acid solution and undergoing similar treatment as in (A). Note that only half of the particles showed a truncated tetragonal bipyramidal shape.

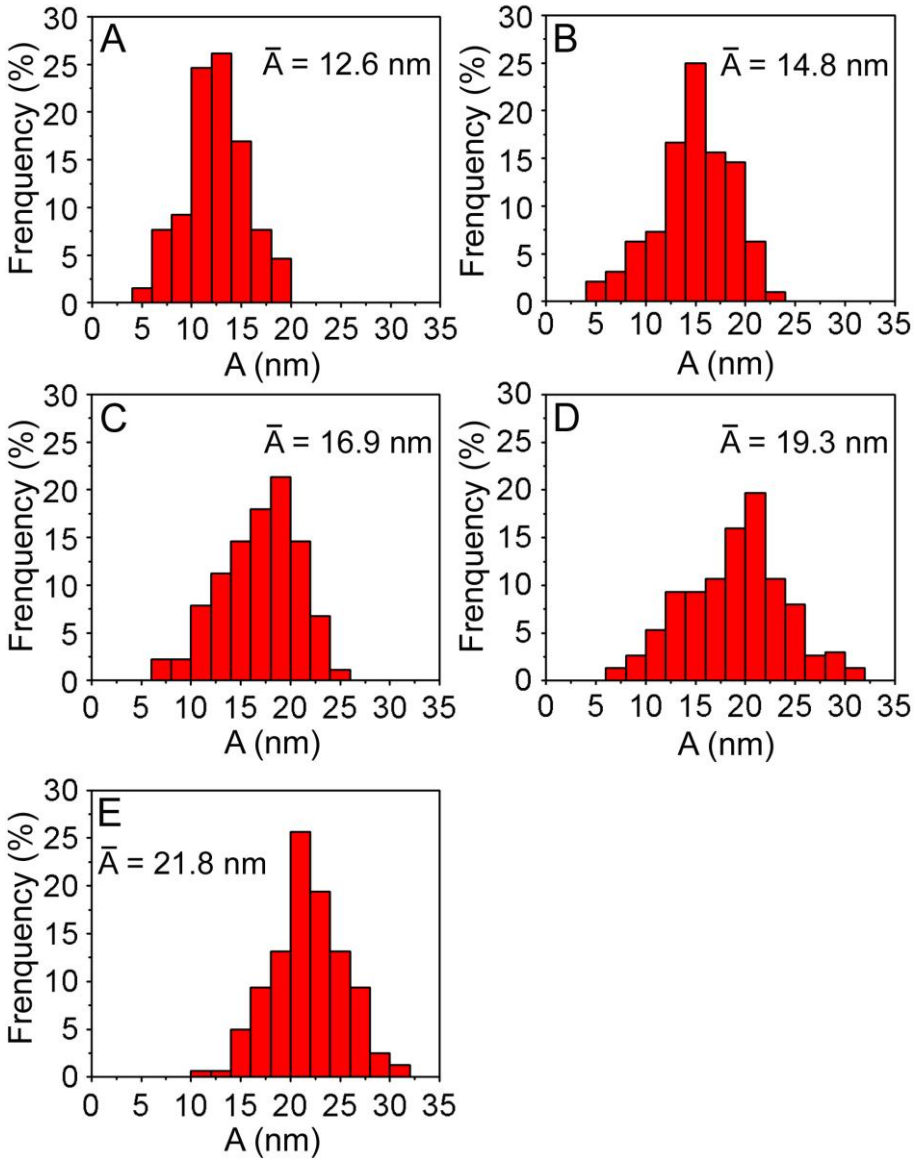

Figure S3. The average edge length *A* at different hydrothermal treatment times: (A) 4 h, (B) 8 h, (C) 13 h, (D) 16 h, and (E) 20 h.

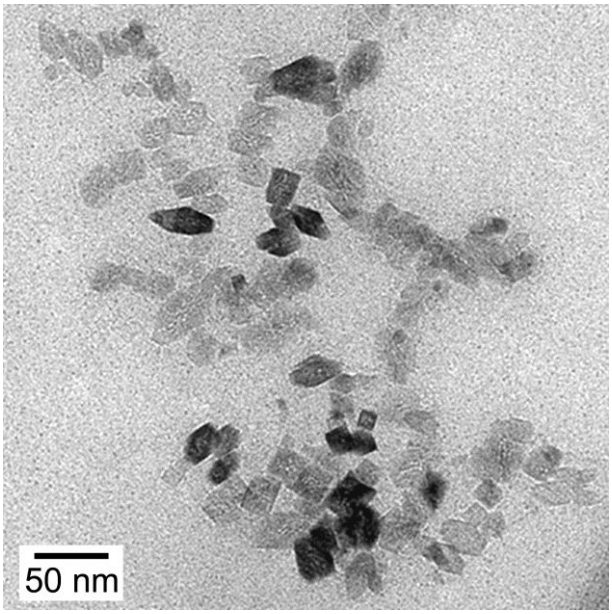

Figure S4. TEM image of anatase TiO_2 nanocrystals obtained by hydrothermal treatment at 120 ^{o}C. The nanocrystals with an average edge length *A* of 17.6 nm are smaller than those prepared at 150 ^{o}C (21.8 nm).