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Supplementary Information

Multiple Twinning Drives Nanoscale Hyper-Branching of Titanium Dioxide Nanocrystals

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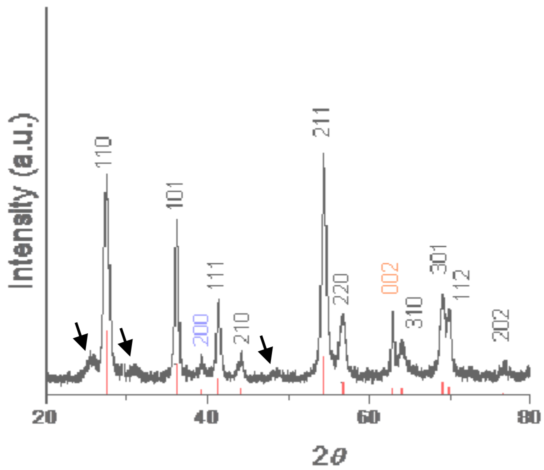
X-ray diffraction (XRD) analyses of hyper-branched TiO_2 nanocrystals

Diffraction patterns obtained well match a known XRD pattern of rutile TiO_2 (red vertical lines JCPDS # 21-1276). The stronger intensity ratio of (002)/(110) diffraction of 0.37 compared to bulk TiO_2 with the intensity ratio of 0.10 support the anisotropic growth of nanorods along the (002) axis.



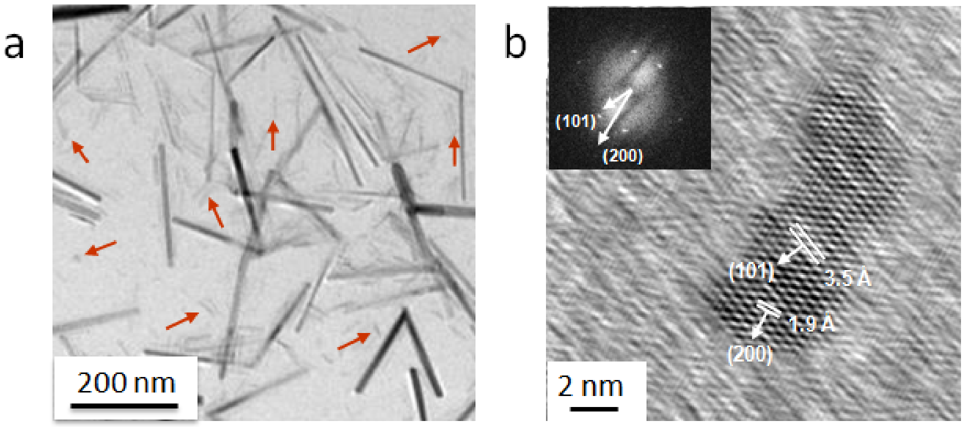
Supplementary Figure 1. X-ray diffraction patterns of hyper-branched rutile-phase TiO_2 nanowires. Resulting products still contains small portion of anatase-phase short rods (black arrows).

Synthesis of hyper-branched TiO_2 nanowires.

Under inert conditions, titanium chloride (0.5 mmol) and oleylamine (6.0 mmol) were mixed in 3 neck round bottom flask equipped with a reflux condenser and a thermocouple and heated up to 245 ^oC. As the temperature increases, the colorless reaction solution turns to dark blue solution indicating complexation of titanium chloride with oleylamine. Then, an appropriate amount of oleic acid was rapidly injected into the solution and the resulting solution was further heated up to 275 ^oC. After 2 min, the reaction mixture was quickly quenched by adding an excess amount of cold toluene. The multiply branched wires were separated by centrifugation at 1500 r.p.m and redispersed in toluene. Control of the degree of branching was possible by varying the amount of oleic acid used. To obtain bipods and tripods as major products, 0.5 mmol of oleic acid was employed. For the nanowires with higher degree of branching, 1.0 mmol of oleic acid was used. For the hyper-branched thick rods, 2.0 mmol of oleic acid was employed

Structure information of TiO_2 nanocrystals.

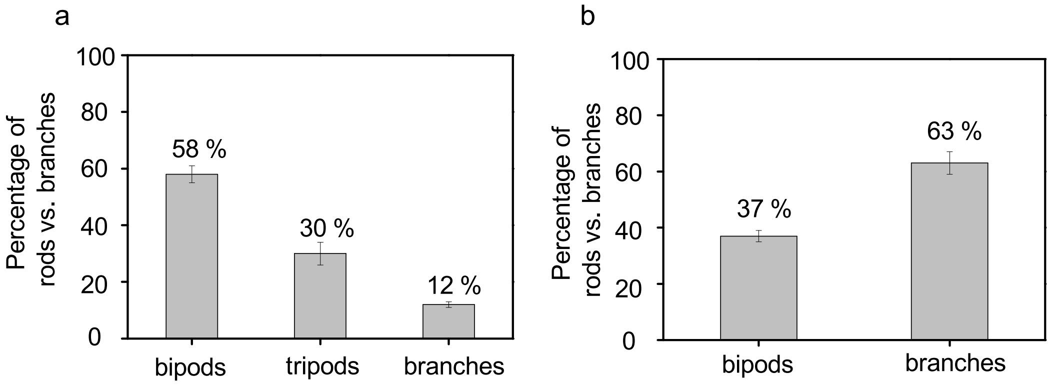
As-synthesized TiO_2 nanocrystals were deposited from their toluene dispersion on a carbon TEM grid by drop casting method. The HR-TEM studies clear show that lattice fringes of 3.5 Å and 1.9 Å are consistent with the (101) and (200) planes of anatase-phase short rod (Figure S2b, JCPDS card # 21-1272).



Supplementary Figure 2. TEM images of TiO_2 nanocrystals. a) low-magnification image of a mixture of anatase-phase (red arrows) and rutile-phase TiO_2 nanocrystals. b) HR-TEM image and FFT pattern (inset) of an anatase nanocrystal.

Comparison of percentages between branched and un-branched TiO_2

Below diagrams show the percentage of rods *vs*. branches. The values are obtained from the statistical analyses of typically 50 digital images. The error bars indicate the standard deviation.



Supplementary Figure 3. The distribution diagrams of TiO_2 nanocrystals prepared by using a) 0.5 mmol and b) 1.0 mmol of oleic acid. When amount of oleic acid is increased, the degree of branching of TiO_2 is increased from 12 % to 63 %.