Electronic Supplementary Information (ESI)

Green synthesis of shape-defined anatase TiO_2 nanocrystals wholly exposed with {001} and {100} facets

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Experimental Section

1. Synthesis of TiO_2 samples.

Vermiculite (VMT) is a natural clay mineral, composed of an $MgO_2(OH)_4$ octahedra sheet symmetrically coupled to an octahedral sheet of silica, and has a net negative charges originated from isomorphic substitution of Al^{3+} in the Si^{4+} sites of the tetrahedral sheets which are balanced by some interlayer cations.[1] The acid-delaminated vermiculite (DVMT) was prepared according to a protocol as previously reported.[2] The as-received vermiculite (100 g, 300 mesh) was dispersed into 4L of a 2 M HCl solution and the resulting slurry was magnetically stirred for 8 h. The vermiculite was then separated by filtering and washed thoroughly with deionized water several times until the filtrate had a pH value of 7.0. Following this, the obtained solid material was dried at 100 °C for 12 h. The final product after grinding was a fine powder that was whiter than the starting VMT.

The DVMT powders were dispersed in 150 mL deionized water under magnetic stirring for 30 min at room temperature. Following the addition of tetramethylammonium hydroxide (Me_4NOH, 0.488 mL, 25%, Tianjin Guangfu Fine Chemical Research Institute) solution, a solution of titanium isopropoxide (TTIP, 0.348 mL, 97%, Sigma-Aldrich) in 2-propanol (10 mL, 99.5%, Sigma-Aldrich) was added dropwise under vigorous stirring. After the suspension was stirred further for 10 min, it was transferred into an autoclave and maintained at 180 °C for 10 h and then cooled to room temperature naturally. The DVMT layers were separated from the mixture containing TiO_2 and solution at lower rotating speed of centrifugation and the TiO_2 nancrystals were remained in the solution because the DVMT layers still have large two-dimensional size (micron order) after the reaction. Subsequently, the TiO_2 nanocrystals were collected by higher speed centrifugation, washed with deionized water and absolute ethanol several times, and dried in a vacuum at 60 °C for 12 h. Controllable morphology and size of TiO_2 were achieved by adjusting the ratio of DVMT to TTIP in the reaction system (from 0, 20, 40, to 80 g DVMT per molar TTIP were employed, corresponding to the nominal weight ratio of DVMT to TiO_2: 0, 0.25, 0.5, and 1, respectively).

2. Characterization.

X-ray diffraction (XRD) patterns were recorded using a D8 Advance X-ray diffractometer (Bruker, Germany) (40 kV, 40 mA) with nickel-filtered Cu Kα radiation (λ = 1.54056 Å). The morphology of the samples was observed with field-emission scanning electron microscopy (FE-SEM, Zeiss Supra55VP, Japan) using an In-Lens detector operated at an accelerating voltage of 20 kV. Elemental analysis was carried out by energy dispersive spectroscopy (EDS), and the EDS spectra were obtained using a Zeiss Supra55VP SEM instrument equipped with an EDS detector (Bruker, X-flash-sdd-5010, Germany). High resolution transmission electron microscopy observation was carried out using a JEM-2010F (HRTEM, JEOL, Japan) operated at 200 kV. Fourier transform infrared

spectroscopy (FTIR) measurements were conducted on a BIO-RAD FTS 165 instrument at a resolution of 4 cm^{-1} using KBr for dilution.

References:

1 M. F. Brigatti, E. Galan and B. K. G. Theng, in *Handbook of Clay Science, Developments in Clay Science*, ed. F. Bergaya, B. K. G. Theng and G. Lagaly, Elsevier, Amsterdam, 2006, Vol. 1, ch. 2, pp. 43-44.

2 S. C. Tjong, Y. Z. Meng and A. S. Hay, *Chem. Mater.*, 2002, **14**, 44.

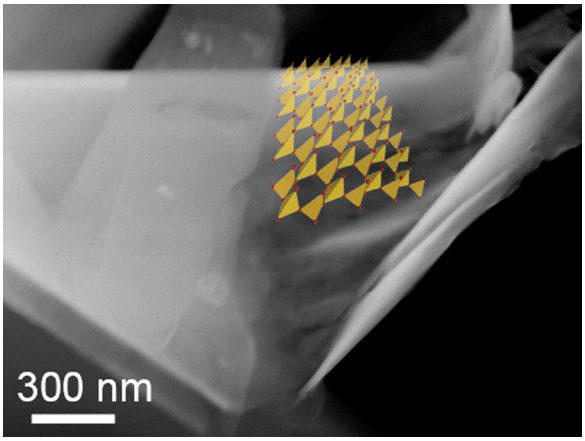

Fig. S1 High-magnification SEM image of DVMT, and the surface structure of DVMT layers (inset).

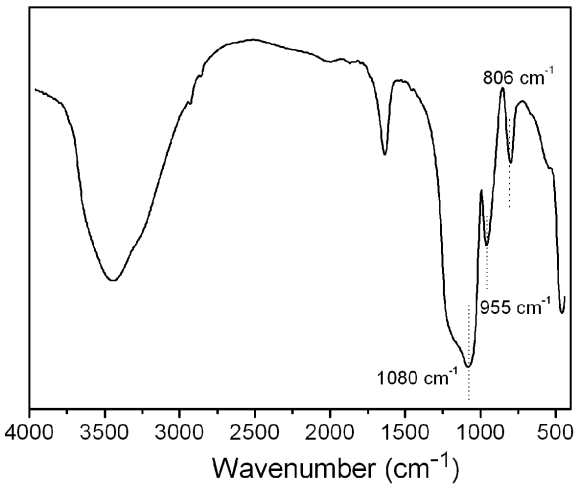

Fig. S2 FTIR spectra of the DVMT sample. Absorption bands at 1080, 806 and 460 cm^{-1} originated from the stretching and bending vibrations of SiO_4 tetrahedra, and the band at 955 cm^{-1} originated from the stretching vibration of Si-OH groups on the surface of DVMT layers.

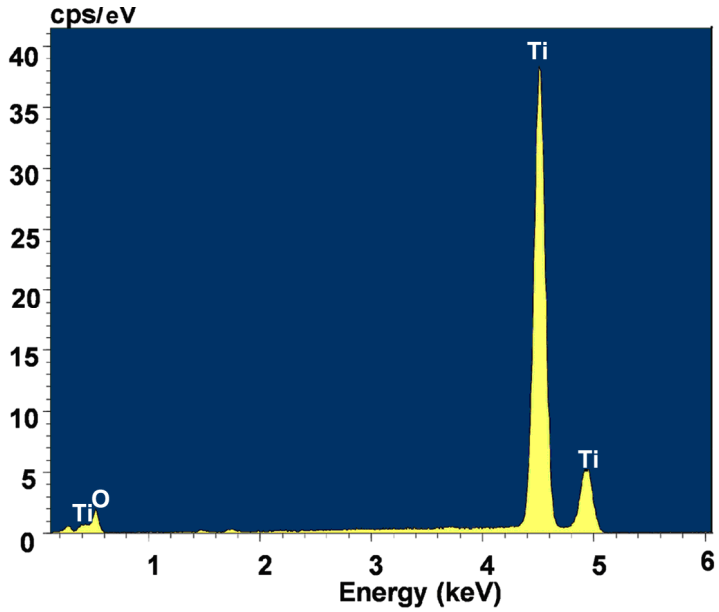

Fig. S3 EDS analysis of the anatase TiO_2 nanocuboids obtained in the system with DVMT to TTIP ratio of 40 g mol^{-1}.

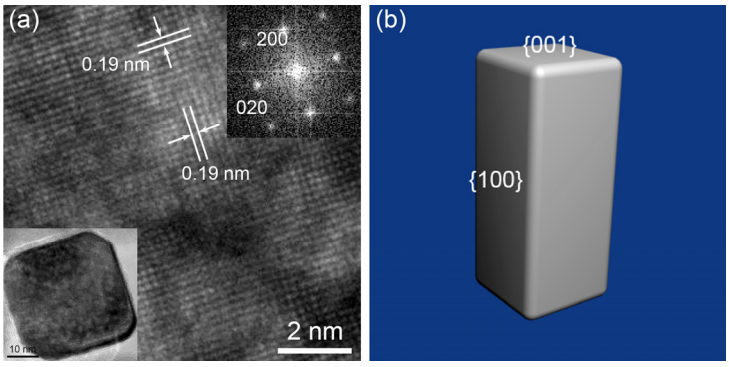

Fig. S4 (a) Top view HRTEM images recorded from another standing TiO_2 nanocuboid single crystal with [001] orientation, and corresponding FFT pattern (inset). (b) Schematic morphology of a single anatase TiO_2 nanocuboid obtained in the system with DVMT to TTIP ratio of 40 g mol^{-1}.

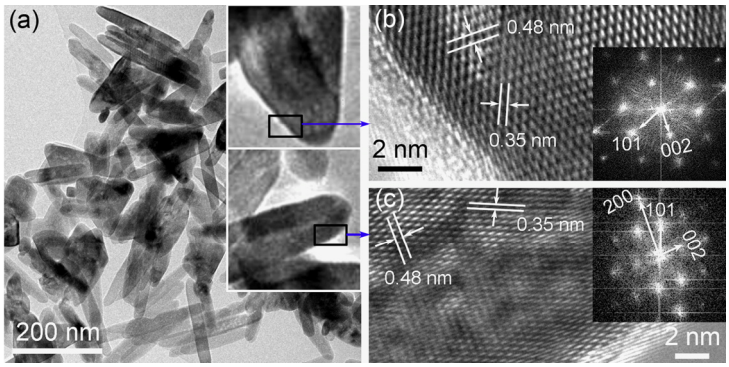

Fig. S5 (a) TEM images of TiO_2 nancrystals obtained in the system with DVMT to TTIP ratio of 0 g mol^{-1}. (b, c) HRTEM images taken from parts of (a) marked by the rectangles, respectively. Insets are the corresponding FFT patterns.

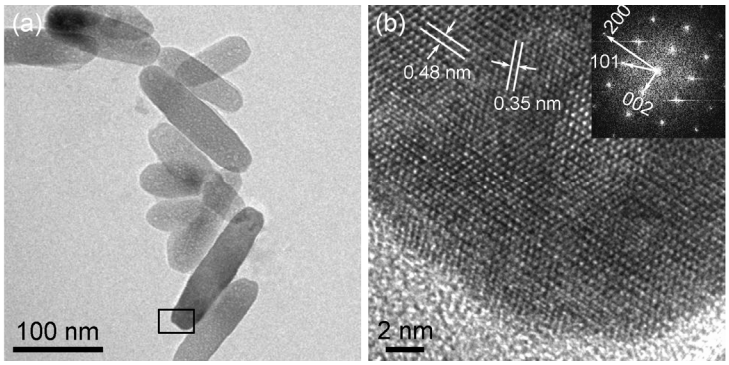

Fig. S6 (a) TEM image of TiO_2 nancrystals obtained in the system with DVMT to TTIP ratio of 20 g mol^{-1}. (b) HRTEM image taken from part of (a) marked by the rectangle. Inset is the corresponding FFT pattern.

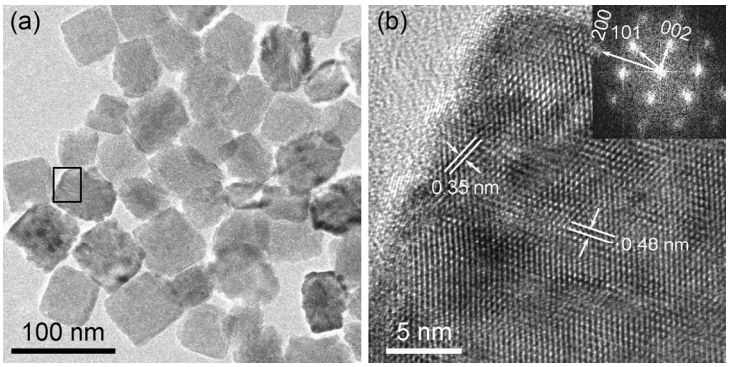

Fig. S7 (a) TEM image of TiO_2 nancrystals obtained in the system with DVMT to TTIP ratio of 80 g mol^{-1}. (b) HRTEM image taken from part of (a) marked by the rectangle. Inset is the corresponding FFT pattern.

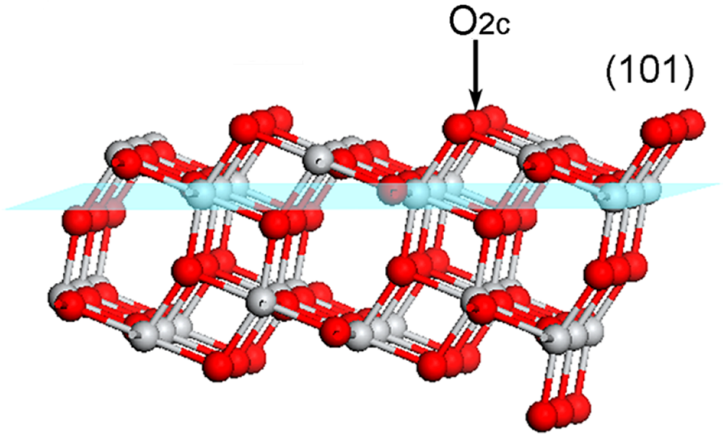

Fig. S8 (101) surface of anatase TiO_2, and Ti and O atoms are represented by grey and red spheres, respectively. (O_{2c} refers to two fold O).

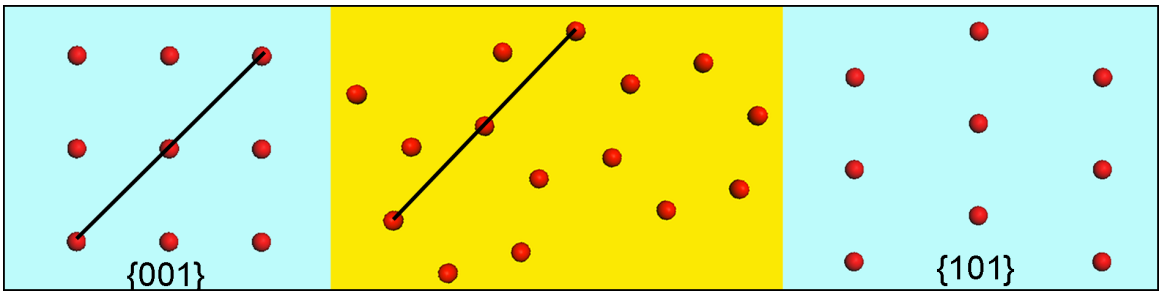

Fig. S9 Top view of O_a atoms on the surface of DVMT layer (*yellow*) and O_{2c} atoms on the (001) and (101) planes of anatase TiO_2 (*green*), respectively.