Supporting Information

A selective etching phenomenon on {001} faceted anatase titanium dioxide single crystal surface by hydrofluoric acid

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(I) *Experimental Section*

Synthesis. Anatase TiO_2 single crystals were synthesized through a facile low temperature hydrothermal method. Hydrochloric acid (HCl, 1.5 M) was used to adjust the pH of deionized water (1.0 L) to around 2.0. A 0.02 M TiF_4 (Aldrich Chemical) stock solution was prepared by dissolving TiF_4 in pH adjusted deionized water. Solutions containing 4.5, 5.2, 8.3, and 10.6 mM of TiF_4 were prepared by dilution of the stock solution with deionized water (Millipore Corp., 18 MΩ cm) and all resultant solutions were adjusted to pH of ca. 1.52 by 0.1 M of HCl solution. In a typical synthesis, a 50 mL of TiF_4 solution with different concentrations was added to a Teflon-lined autoclave, and kept at 180 ºC for 15 h in an oven. After hydrothermal reaction, the products were collected by centrifugal separation and carefully washed with deionized water, and then dried in a nitrogen stream.

Characterization. The obtained products were comprehensively characterized by SEM (JSM-6300F), TEM (Philips F20), and XRD (Shimadzu XRD-6000 diffractometer).

(Π) *Theoretical Calculations*

The anatase (001) surface was modeled by a slab with the (2×1) surface cell comprising an 18 atomic layers and a total of 36 atoms separated by a vacuum region of 10 Å. The anatase (101) surface was modeled by a slab with the (1×1) surface cell comprising a 24 atomic layers and a total of 36 atoms. When the geometry was optimized, the adsorbates and the atoms in the top 12 atomic layers of the (001) surface or in the top 16 atomic layers of the (101) surface were allowed to relax, while the rest bottom layers of the surfaces were fixed at the ideal bulk-like position (using the theoretical lattice constant $a = 3.80$ Å, and $c/a = 2.535$). For the isolated molecules, a cubic unit cell with the lattice constant as 15.0 Å was used to accommodate one molecule in the calculations.

All computations were performed using the Quantum Espesso (QE) software. Electron-ion interactions were described using the ultrasoft pseudopotentials.[1] Valence states include the Ti 3*s*, 3*p*, 3*d*, and 4*s* states, the O 2*s* and 2*p* states, the F 2*s* and 2*p* states, and the H 1*s* shell. A plane-wave basis set was employed with a kinetic energy cut-off of 408.17 eV (30Ry) and augmented density cutoff of 4081.7 eV (300Ry). For the electron-electron exchange and correlation interactions, the functional of Perdew, Burke and Ernzerhof (PBE),[2] a form of the general gradient approximation (GGA), was used throughout. We performed Brillouin-zone integrations using Monkhorst-Pack grids of special points. (2×4×1) k-point meshes were employed for the (101) (1×1) surface cell and (001) (2×1) surface cells, respectively. Our selected kinetic energy cut-off and density of k-point mesh were similar as the previous theoretical studies.[3-5]

The reaction energy shown in Fig. 3 in the manuscript was calculated based on the following equation:

$$\Delta E = \sum E_{\mathrm{product}} - \sum E_{\mathrm{reagent}}$$

where, E_{product} is the energy of products, and E_{reagent} is the energy of reagents in each reaction.[6] The bond length and angles shown in Fig. 3 in the manuscript were calculated based on the DFT optimized structure of the systems.

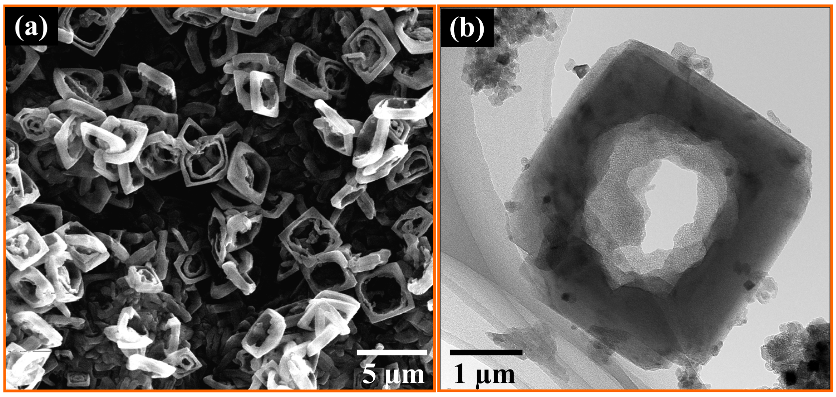

Fig. S1 (a) low magnification SEM image of anatase TiO_2 single crystals after 40 hours of reaction in 10.6 mM of TiF_4 solution (pH = 1.52) at 180 ºC. (b) TEM image of an individual anatase TiO_2 single crystal ring formed by the remaining {101} facets.

References:

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