# **Supporting Information**

### On the Synergistic Effect of Hydrohalic Acides in the Shape-controlled Synthesis of Anatase TiO<sub>2</sub> Single Crystals

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## **Experimental Section**

Titanium(IV) tetrachloride (TiCl<sub>4</sub>), hydrochloric acid (HCl, 25% w/w) and hydrofluoric acid (HF, Sigma-Aldrich, 48%, ACS reagent) were used as the precursor and capping agent, respectively. Firstly, aqueous TiCl<sub>4</sub> was dissolved in HCl to a concentration of 0.15 M. Then in a typical synthesis, 29 mL of deionized water and 0.4 mL of HF (10 wt%) was added into a 50 mL Teflon–lined autoclave. Then 1 mL of 0.15M TiCl<sub>4</sub> was dripped into the reactor to form a transparent mixture. After that, the reactor was transferred into a stainless steel autoclave and heated at 120-200 °C for 3 – 18 h in an oven. The resulting product was separated through centrifugation process and washed with deionized water for three times.

## **Materials Characterization**

Crystallographic information of anatase TiO<sub>2</sub> single crystals was obtained with X-ray diffraction (XRD, Bruker D8 Advanced Diffractometer, Cu Kα radiation, 40 kV). The morphology and structure of the samples were characterized by high-resolution transmission microscopy and selected area electron electron diffraction (HRTEM/SAED, JEOL JEM-2010F), and field emission scanning electron microscopy (FESEM, HITACHI S4800 and SEM, JOEL JSM 6380). Chemical composition and the binding energies of the elements on the surface of anatase  $TiO_2$ single crystals were analyzed using X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD, Al Ka radiation). All binding energies were referenced to the C1s peak (284.8 eV) arising from surface hydrocarbons (or possible adventitious hydrocarbon). Regarding the sampling process, samples washed with ethanol were redispersed in ethanol and dropped on a conductive SEM sample holder or a carbon-coated copper grid with irregular holes for TEM analysis. Samples for XPS analysis were prepared by drying the washed products at 60 °C overnight.

### **Computational details**

Density functional theory (DFT) calculations have been performed with the PWScf code,<sup>[1]</sup> which is part of the Quantum-Espresso package. The plane-wave basis set cut-offs for the smooth part of the wavefunctions and the augumented density were 25 and 200 Ry, respectively. Electron-ion interactions were described by ultrasoft pseudopotentials, with electrons from O, F 2s, 2p, Cl 3s, 3p and Ti 3s, 3p, 3d, 4s shells were explicitly included in the calculations.<sup>[2]</sup> Anatase TiO<sub>2</sub> surfaces were modeled by periodic slabs. In adsorption energy calculations, the primary 1×1 surface cells were used for all the three (101), (100) and (001) slabs, which contain 4, 9 and 6 layers, respectively. The adsorption was modelled on both sides of the slab. To estimate the solvation energies of HF/HCl covered surfaces and the reaction energies of the replacement reactions (Scheme S1), we also used 1×2 surface cell for (001) for consistence, i.e., four HCl or HF molecules can adsorb in each surface cell at all the three surfaces.

The adsorption energies ( $E_a$ , see Table 1) of dissociated HCl and HF at the anatase TiO<sub>2</sub> surfaces were first calculated by using the following equation,

 $E_{a} = -(E_{surf+mol} - nE_{mol} - E_{surf})/n$ (1)

in which  $E_{surf}$  is the total energy of the TiO<sub>2</sub> slab,  $E_{mol}$  is the total energy of the adsorbed molecule (HCl or HF) in gas phase,  $E_{surf+mol}$  is the total energy of the system with adsorbed molecules at the surface, and n is the number of the adsorbed molecules in each surface cell (four at (101) and (100), and two at (001)).

The surface energies of clean anatase  $TiO_2(101)$ , (100) and (001) surfaces were taken from an early DFT studies by one the authors of the current work,<sup>[3]</sup> which employed nearly the same set of calculation settings and code. To quantitatively estimate the effect of adsorbed HCl or HF on the surface energies in the solution, we then calculated the adsorption energies of HCl and HF by using the following equation,

$$E_a = -[(E_{surf+mol} + E_{ad-sol}) - n(E_{mol} + E_{mol-sol}) - E_{surf}]/n$$
(2)

in which  $E_{ad-sol}$  and  $E_{mol-sol}$  are the solvation energies of the HCl (or HF)-covered slabs and a single HCl or HF molecule, respectively. Specifically, calculations for  $E_{mol-sol}$ were performed employing the Gaussian 03 computational software package.<sup>[4]</sup> PBEPBE correlation functional<sup>[5,6]</sup> in combination with the 6-311++G(d,p) basis set<sup>7</sup> were used. The polarizable continuum model (PCM)<sup>[8,9]</sup> was employed to include solvent (H<sub>2</sub>O) effects. In order to estimate  $E_{ad-sol}$ , we used the SIESTA code<sup>[10]</sup> and the surface structures directly obtained from PWScf calculations. The long-range electrostatic solvation effect for the systems in aqueous surroundings are taken into account by using a periodic continuum solvation model based on the modified Poisson-Boltzmann equation (CM-MPB).<sup>[11-13]</sup>

 Table S1 Calculated solvation energies of HCl and HF molecules.

	Solvation energy/eV		
HF	-0.33		
HCl	-0.26		

**Table S2** Calculated solvation energies (in eV) of different clean and HCl/HF-coved surfaces.

	Clean	HF	HCl
(001)	-0.836	-0.456	-0.349
(100)	-0.855	-1.087	-0.94
(101)	-0.838	-0.788	-0.592

**Table S3** Calculated adsorption energies ( $E_a$ , in eV) of HCl and HF at the different surfaces in solution by using the equation (2).

	(001)	(100)	(101)
HF	1.11	1.15	1.12
HCl	0.59	0.69	0.69

**Table S4** Calculated formation energies ( $\gamma$ ), the total adsorption energies ( $E_a$ <sup>'</sup> in J·m<sup>-2</sup>, Note:  $E_a$ <sup>''</sup> is obtained with the  $E_a$  of (101) as the reference) and the updated formation energies ( $\gamma'$ ,  $\gamma'=\gamma-E_a'$ ) of the anatase TiO<sub>2</sub>(101), (100) and (001) surfaces (in J·m<sup>-2</sup>). HCl at (101) and HF at (100) and (001) are considered.

	(101)	(100)	(001)
γ	0.44	0.53	0.9
E <sub>a</sub> '	0.56 (HCl)	1.00 (HF)	1.24 (HF)
<b>E</b> <sub>a</sub> "	0	0.44	0.68
γ'	0.44	0.09	0.22

**Table S5** Calculated formation energies ( $\gamma$ ), the total adsorption energies ( $E_a$ <sup>'</sup> in J·m<sup>-2</sup>, Note:  $E_a$ <sup>''</sup> is obtained with the  $E_a$  of (101) as the reference) and the updated formation energies ( $\gamma'$ ,  $\gamma'=\gamma-E_a$ <sup>'</sup>) of the anatase TiO<sub>2</sub>(101), (100) and (001) surfaces (in J·m<sup>-2</sup>). HCl at (101), (100) and (001) are considered.

	(101)	(100)	(001)
γ	0.44	0.53	0.9
E <sub>a</sub> '	0.56 (HCl)	0.6 (HCl)	0.66 (HCl)
Ea"	0	0.04	0.1
γ'	0.44	0.49	0.8

**Table S6** Calculated formation energies ( $\gamma$ ), the total adsorption energies ( $E_a$ <sup>'</sup> in J·m<sup>-2</sup>, Note:  $E_a$ <sup>''</sup> is obtained with the  $E_a$  of (101) as the reference) and the updated formation energies ( $\gamma'$ ,  $\gamma'=\gamma-E_a$ <sup>'</sup>) of the anatase TiO<sub>2</sub>(101), (100) and (001) surfaces (in J·m<sup>-2</sup>). HF at (101), (100) and (001) are considered.

	(101)	(100)	(001)
γ	0.44	0.53	0.9
E <sub>a</sub> '	0.91 (HF)	1.00 (HF)	1.24 (HF)
E <sub>a</sub> "	0	0.09	0.33
γ'	0.44	0.44	0.57

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**Scheme S1** Replacement reaction of surface HCl by HF in solution. (Note: 4 HF or HCl molecules are considered since altogether 4 dissociated molecules adsorb on the two sides of the slab.)



Fig. S1 XRD pattern of the as-obtained anatase  $TiO_2$  crystals dominated with {001} and {100} facets. The sample is in a pure anatase phase without rutile or bookite inpurity.



Fig. S2 XPS spectra of the anatase  $TiO_2$  synthesized at 160 °C for 14 h. (left: unwashed sample; right: washed sample)



Fig. S3 Low-magnification SEM images of the anantase  $TiO_2$  single crystals synthesized at 160 °C for 3h(a) and 14h(b).



**Fig. S4** 2-D and 3-D (incert) Wulff construction diagrams of the anatase  $TiO_2$  crystals using the surface energies of (a) HCl- and (b) HF- covered facets, and (c) HCl-covered {101} and HF-covered {100} and {001} facets in solution.



Fig. S5 HRTEM and SEM images of the anantase  $TiO_2$  single crystals. (a)  $TiO_2$  nanocrystals with large percent of {101} facets prepared with  $TiCl_4$  and HCl and (b)  $TiO_2$  single crystals with large percent of {001} facets synthesized with  $TiF_4$  and HF.