

# Free Energies of Low-Indexed Surfaces of Anatase and Rutile TiO<sub>2</sub> Terminated by Non-metals

C.H. Sun<sup>\*,\*\*</sup>, H.G. Yang<sup>\*</sup>, S. Smith<sup>\*\*\*</sup>, Q.S. Zhang<sup>\*</sup>, G. Liu<sup>\*</sup>, J. Zou<sup>\*\*\*</sup>, H.M. Cheng<sup>\*\*\*\*</sup>, G.Q. Lu<sup>\*</sup>

<sup>\*</sup>ARC Centre of Excellence for Functional Nanomaterials, School of Engineering and Australian Institute of Bioengineering and Nanotechnology, The University of Queensland, QLD 4072, Australia  
maxlu@uq.edu.au

<sup>\*\*</sup>Centre for Computational Molecular Science, Biological and Chemical Sciences Faculty and Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, QLD 4072, Australia, s.smith@uq.edu.au

<sup>\*\*\*</sup>Centre for Microscopy and Microanalysis, The University of Queensland, QLD 4072, Australia,

<sup>\*\*\*\*</sup>Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China

## ABSTRACT

The structures and free energies ( $\gamma$ ) of low index surfaces of anatase and rutile TiO<sub>2</sub> terminated by nonmetals (H, B, C, N, O, F, Si, P, S, Cl, Br, and I) have been studied with the frameworks of density functional theory. It is found that, (i) the surface chemistry and stabilities can be adjusted using different nonmetal adsorbates; and (ii) the relative stabilities of these low-indexed surfaces of both anatase and rutile TiO<sub>2</sub> vary with the adsorbates, indicating that specific surfaces (such as highly reactive surfaces) are obtainable with use of different precursor and crystallographic controlling agents. The above calculated results may serve as a guideline for the synthesis of various metal oxides.

**Keywords:** TiO<sub>2</sub>, anatase, rutile, surface free energy, surface stability

## 1 INTRODUCTION

The current interest in titanium dioxide (TiO<sub>2</sub>) for advanced photochemical applications has prompted a number of studies to analyze its surface stability and reactivity with an aim to synthesize highly active surfaces [1-3]. Unfortunately, surfaces with high reactivity usually diminish rapidly during the crystal growth process as a result of the minimization of surface energy. So it is an open challenge to synthesize highly active surfaces through controlling their surface chemistry. For instance, in the case of anatase TiO<sub>2</sub>, (101) is the most stable and frequently observed surface amongst various low-index surfaces, due to its relatively low surface free energy ( $\gamma=0.44$  J/m<sup>2</sup> [4]). However, the high stability/low reactivity of the majority (101) surface makes it often difficult to understand the observed reactivity of anatase. A typical example is that recent sum frequency generation studies of the coadsorption of water and methanol on anatase nanoparticles show the presence of hydroxyls and methoxy groups, with the latter

being strongly bound to the surface and capable of replacing surface hydroxyls [5-6]. This cannot be result from (101) surfaces - on which both water and methanol can only be molecularly adsorbed [7-9]. Gong et al. believed that the minority (001) surface exhibits a high reactivity and can account for the above results based on detailed density functional theory (DFT) calculations [10]. Thereby, anatase TiO<sub>2</sub> single crystals with a large percentage of {001} facets are predicted to have high reactivity, which underlines the importance of developing effective approaches to control the stabilities of different surfaces.

Typically, the PH value is a decisive factor for controlling the final sample size and shape [11-12]. However, both hydrated (acid) and oxygenated (basic) surfaces show higher surface free energies than clean conditions [13-14], which is not helpful for the stabilization of highly reactive surfaces. High  $\gamma$  for H- and O-terminated surfaces are mainly caused by the high bonding energies ( $D_0$ ) of H-H (436.0 kJ/mol) and O-O (498.4 kJ/mol) [15]. Therefore, to find a low  $D_0$  element with high bonding to Ti might be a solution for stabilizing the faceted surfaces. In this paper, we carried out systematic investigation of 12 non-metallic atoms X (X= H, B, C, N, O, F, Si, P, S, Cl, Br, I) using first-principle quantum chemical calculations, in which clean surfaces of (001), (101) and (100) were used as references. Based on such calculations, it is found that adsorbate atoms can effectively change the relative stabilities of different crystal facet, which may serve as a guideline for the selecting of morphology controlling agent for experimental synthesis.

## 2 COMPUTATIONAL METHODS

In each case, stoichiometric slab models (1 $\times$ 1), consisting at least 6 atomic layers, are employed. In clean situations, all low-indexed surface contain fivefold Ti on two sides of each slab, which is saturated by X (X=H, B,

C, N, O, F, Si, P, S, Cl, Br, I). During the structural optimization, all atoms are relaxed without any constraint before the total energies are calculated. All calculations have been carried out using density functional theory (DFT) within the generalized-gradient approximation (GGA) [16], with the exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE) [17-18]. This has been implemented in the Vienna ab initio simulation package (VASP) [19-20], which spans reciprocal space with a plane-wave basis, in this case up to a kinetic energy cutoff of 450 eV.

### 3 RESULTS AND DISCUSSION

#### 3.1 Anatase TiO<sub>2</sub>

According to early experimental studies, the surface of anatase TiO<sub>2</sub> with the equilibrium morphology consists of two facets, {001} and {101}, whose surface free energies are calculated. The calculated values of surface free energies of (001) and (101) of anatase TiO<sub>2</sub> terminated by different adsorbates are listed in Table 1. Based on these results, it is found that: (i) among 12 non-metal-terminated surfaces and the clean surfaces, the surfaces terminated by different nonmetals present different surface free energies, suggesting that the surface chemistry and stabilities can be adjusted using different nonmetal adsorbates; and (ii) the relative stabilities of (001) and (101) vary with the adsorbates. Although in most cases, (101) is more stable than (001), however, with the termination of Si and F, (001) is more stable, indicating that the percentages of these surfaces may be controllable using suitable morphology controlling agents.

X	(001)	(101)
Clean	0.92	0.39
H	3.76	3.11
B	1.47	-0.21
C	4.18	1.85
N	8.12	6.31
O	2.88	2.46
F	-0.55	-0.22
Si	0.93	1.31
P	3.73	3.25
S	2.84	2.56
Cl	1.61	1.40
Br	1.98	1.92
I	1.18	0.83

Table 1: Calculated surface free energies (in unit of J/m<sup>2</sup>) of (001) and (101) of anatase TiO<sub>2</sub>.

#### 3.2 Rutile TiO<sub>2</sub>

Based on the equilibrium morphology of rutile TiO<sub>2</sub>, four surfaces, including (001), (100), (011) and (110), are studied here. The calculated values of surface free energies for rutile TiO<sub>2</sub> terminated by different adsorbates are listed in Table 2, with clean surfaces being the reference. Similar with anatase TiO<sub>2</sub>, the surface free energies of rutile TiO<sub>2</sub> strongly depend on the surface adsorbates. For instance, the surface free energies of (101) may change from -3.30 J/m<sup>2</sup> (B-terminated) to 9.06 J/m<sup>2</sup> (N-terminated), suggesting that the controlling of the surface adsorbates is an effective way to adjust the surface stability and reactivity in a wide range. Among 12 nonmetals, F and Si can improve the stabilities of all four surfaces investigated. Another interesting feature is the change of the relative stabilities of these surfaces. For clean surfaces, the stability is in the sequence of (110) > (100) > (101) > (001). However, with the coverage of nonmetals, such sequence has been totally changed. Importantly, the highly active surfaces of (001) and (101) present high stabilities when they are terminated by F and B. Following these calculations, large areas of (001) and (101) can be obtainable if the surface of rutile samples is covered by these atoms, which can serve as a guideline for experimentalists focusing on the synthesis of highly active rutile samples.

X	(001)	(100)	(110)	(101)
Clean	1.49	0.60	0.27	1.10
H	1.46	3.71	2.56	1.81
B	0.41	-0.97	0.61	-3.30
C	0.44	2.06	2.80	1.77
N	9.80	9.10	5.87	9.06
O	1.14	3.21	2.26	2.85
F	-0.76	-0.33	-0.24	-0.69
Si	-1.26	-0.22	0.20	-1.51
P	1.39	2.99	2.11	1.01
S	0.85	2.16	1.42	1.87
Cl	1.49	1.35	0.80	1.18
Br	2.54	1.35	0.82	1.71
I	1.75	0.56	0.34	0.71

Table 2: Calculated surface free energies (in unit of J/m<sup>2</sup>) of (001), (100), (110) and (101) of rutile TiO<sub>2</sub>.

### 4 CONCLUSIONS

The surface free energies of anatase and rutile TiO<sub>2</sub> have been calculated with the frameworks of density functional theory with the exchange-correlation functional of GGA. Two conclusions can be summarized from our calculations: (i) the surface chemistry and stabilities can be adjusted using different nonmetal adsorbates; and (ii) the relative stabilities of these low-indexed surfaces of both anatase and rutile TiO<sub>2</sub> vary with the adsorbates. The above conclusions indicate that the controlling of the surface

adsorbates is an effective way to adjust the surface stability and reactivity in a wide range, which is of fundamental importance for the control synthesis of TiO<sub>2</sub>.

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