{001} facets dominated anatase TiO$_2$: Morphology, formation/etching mechanisms and performance

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Controllable growth of anatase TiO$_2$ crystals with exposed high reactive crystal facets has aroused great attention in the fields of science and technology due to their unique structure-dependent properties. Recently, much effort has been paid to synthesize anatase TiO$_2$ crystals with exposed high reactive {001} facets. Herein, we review the recent progress in synthesizing {001} facets dominated anatase TiO$_2$ crystals with different morphologies by various synthetic methods. Furthermore, our review is mainly focused on the formation/etching mechanisms of {001} facets dominated anatase TiO$_2$ crystals based on our and other studies. The extensive application potentials of the anatase TiO$_2$ crystals with exposed {001} facets have been summarized in this review such as photocatalysis, photoelectrocatalysis, solar energy conversion, lithium ion battery, and hydrogen generation. Based on the current studies, we give some perspectives on the research topic. We believe that this comprehensive review on anatase TiO$_2$ crystals with high reactive {001} facets can further promote the relative research in this field.

anatase TiO$_2$, high reactive {001} facets, crystal growth, formation/etching mechanisms, hydrothermal synthesis

1 Introduction

Controllable growth of metallic and semi-conducting nano-crystals with high reactive facets has attracted great interest in the past decade due to their superior properties in catalysis, photocatalysis, gas sensors, photovoltaics, and lithium ion battery [1–25]. Over the past two decades, titanium dioxide (TiO$_2$) has been the dominant semiconductor photocatalyst owing to its superior photocatalytic activity, low cost, abundant supply, non-toxic nature and high photocorrosion resistance [26–30]. Anatase TiO$_2$ has exhibited excellent properties in photocatalysis and solar energy conversion due to its more negative conduction band edge potential versus rutile TiO$_2$ [30, 31]. However, the performance of anatase TiO$_2$ nanocrystals depends on not only their microstructure, size and composition, but also crystal facets [2–6, 19, 20]. For this, anatase TiO$_2$ nanocrystals with high reactive facets such as {001} facets are still highly desired and pursued in scientific and technological fields. But the growth of {001} facets dominated anatase TiO$_2$ crystals is thermodynamically unfavourable owing to their higher average surface energy (0.90 J/m$^2$) versus that of other anatase crystal facets such as [100] (0.53 J/m$^2$) and [101] (0.44 J/m$^2$) [2, 32]. Therefore, development of a method able to synthesize anatase TiO$_2$ nanocrystals with high reactive facets (e.g., [001] facets) has become a huge challenge in scientific and technological fields. Recently, a breakthrough reported by Lu et al. has solved this issue [6]. Their study demonstrated that surface fluorination can dramatically decrease the {001} faceted surface energy to a level lower than that of the {101} faceted surface, and thus resulting in

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anatase TiO₂ single crystals with 47% exposed [001] facets [6]. Following this breakthrough, much effort has been paid to synthesize anatase TiO₂ crystals with high reactive [001] facets using this surface fluorination concept, such as micrometer-sized anatase TiO₂ single crystals with exposed [001] facets [8, 12, 18, 33, 42, 43]. Mechanistically, all related reports to date have exclusively concluded that surface fluorination of anatase TiO₂ is responsible for lowering the [001] faceted surface energy and preserving the [001] faceted surfaces [6, 8, 12, 18, 33, 34, 42, 43]. However, this surface fluorination concept of anatase TiO₂ is a general conclusion. What is the key species (e.g., F⁻ and HF) for preserving the [001] facets of anatase TiO₂ in the process of surface fluorination and crystal growth, which is highly concerned and critically important for understanding and controlling the growth of [001] facets dominated anatase TiO₂ crystals. In additional, our recent study has found that a selective etching on the [001] facets of anatase TiO₂ can occur under high HF concentration conditions, suggesting the reported mechanistic role of surface fluorination might be lopsided [53]. In these respects, there has been no comprehensive review insightfully illustrating and understanding the surface fluorination/etching mechanisms of [001] facets dominated anatase TiO₂.

Considering several recent papers have reviewed the fabrication of [001] facets dominated anatase TiO₂ crystals using different synthetic strategies [50–52, 54, 55], in this review, we will simply introduce the synthesis of [001] facets dominated anatase TiO₂ with different morphologies such as micrometer-sized single crystals, nanocrystals and microspheres. Most attention will concentrate on the mechanisms of surface fluorination and etching of [001] facets dominated anatase TiO₂ through theoretical and experimental studies made by our and other groups, and the performances of the [001] facets dominated anatase TiO₂ in many applications. We believe that this comprehensive review can add insightful knowledge for designing and controlling the growth of [001] facets dominated anatase TiO₂ for more extensive applications.

2 Morphology of [001] facets dominated anatase TiO₂ crystals

To date, [001] facets dominated anatase TiO₂ crystals have been extensively fabricated by using different synthetic approaches including hydrothermal, solvothermal, nonhydrolytic solvothermal alcoholysis and gas-phase oxidation methods [6, 8, 36, 56]. Reviewing current studies on [001] facets dominated anatase TiO₂, the synthesized anatase crystals mainly focus on three morphologies including micrometer-sized single crystals with exposed [001] facets, microspheres with exposed [001] facets and nanocrystals with exposed [001] facets.

2.1 Micrometer-sized anatase TiO₂ single crystals

For micrometer-sized TiO₂ single crystals, improving the percentage of [001] facets is highly desired due to the high reactivity of [001] faceted surface [8, 33]. Micrometer-sized TiO₂ single crystals with 47% exposed [001] facets were firstly reported by Lu et al. in 2008 (Figure 1(a)) [6]. Subsequently, the percentage of exposed [001] facets was improved to 64% by using a water-2-propanol solvothermal synthetic approach (Figure 1(b)) [8]. By creating a fluorine rich reaction environment, Yu et al. fabricated successfully micrometer-sized TiO₂ single crystals with remarkable 80% exposed [001] facets (Figure 1(c)) [33]. Through adding H₂O₂ into hydrothermal reaction solution, micrometer-sized anatase TiO₂ single crystals with exposed [001] and [110] facets were successfully synthesized by Liu and co-workers, as shown in Figure 1(d) [34]. The [110] faceted surfaces have higher average surface energy (1.09 J/m²) than that (0.90 J/m²) of [001] faceted surfaces [2], which may contribute the improved photocatalytic performance of the anatase TiO₂ single crystals [34]. These mi-

Figure 1 (a) SEM image of micrometer-sized TiO₂ single crystals with 47% exposed [001] facets by Lu et al. [6]. (b) SEM image of micrometer-sized TiO₂ single crystals with 64% exposed [001] facets by Lu et al. [8]. (c) SEM image of micrometer-sized TiO₂ single crystals with 80% exposed [001] facets by Yu et al. [33]. (d) SEM image of micrometer-sized TiO₂ single crystals with exposed [001] and [110] facets by Liu et al. [34].