{001} Faceted Anatase TiO2-Based Composites

Subjects: Others

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For anatase TiO2, the {001} crystal facets are the most reactive because they exhibit unique surface characteristics such as visible light responsiveness, dissociative adsorption, efficient charge separation capabilities and photocatalytic selectivity. In this review, a concise survey of the literature in the field of {001} dominated anatase TiO2 crystals and their composites is presented. Even though the design and morphologically controlled synthesis of TiO2-001 is considered to be a hot spot in scientific research, it still has some drawbacks like its wide band gap and high recombination rate. These drawbacks can easily be overcome by coupling them with other materials to form TiO2-001-based composites. This review focusses on the synthesis, properties and applications of TiO2-001-based composites.

Keywords: high energy TiO facet ; TiO facet ; TiO-graphene composite ; doping ; photocatalysis ; Li-ion battery anode

1. Introduction

The rising demand for energy and the increase in environmental pollution have become extremely serious issues in recent years [1][2]. Harnessing the sun's energy to produce electricity and to remediate environmental pollution through the use of advanced nanomaterials has proven to be a promising solution to the world's energy crisis [3][4]. One of the first technologies that come to mind when discussing solar energy is photocatalysis. Photocatalysis relies on using the sunlight to promote the degradation of organic pollutants [5][6]. Among a wide spectrum of semiconductors, TiO2 is the most efficient photocatalyst due to its chemical stability, non-toxicity, strong oxidizing power, biocompatibility, large surface area, corrosion resistivity and cost effectiveness [7][8][9].

The intense interest in titanium dioxide (TiO 2) as a photocatalyst has spurred the successful synthesis and extensive investigations of a variety of its crystal facets. Exploring the application of the high energetic {001} facets of titania is a recent venture in TiO 2 photocatalysis [10][11][12][13]. A natural anatase crystal typically can exhibit many crystal facets, as shown in **Figure 1** [14][15]. Among them, {001} surfaces are highly desired because they are theoretically predicted to possess more active sites (five coordinated Ti +) and higher surface energy (0.90 J/m 2) relative to other energetically more favorable facets such as {100} 0.53 J/m 2 or {101} 0.44 J/m 2 [16]. Both theoretical and experimental studies demonstrate that the photocatalytic activity of the anatase {001} facets is higher than that of the thermodynamically stable {101} facets [17][18][19]. Apart from photocatalytic studies, many other promising applications such as photo- or electrocatalysis, photoelectrochemical or photovoltaic cells, lithium/sodium ion batteries, Li–S batteries and gas sensing can be significantly improved by morphological control and specifically exposed {001} facets on the surface [20][21][22][23]. Hence, more efforts are being made to synthesize TiO 2 nanomaterials with dominant high-energy {001} facets (TiO 2-001).

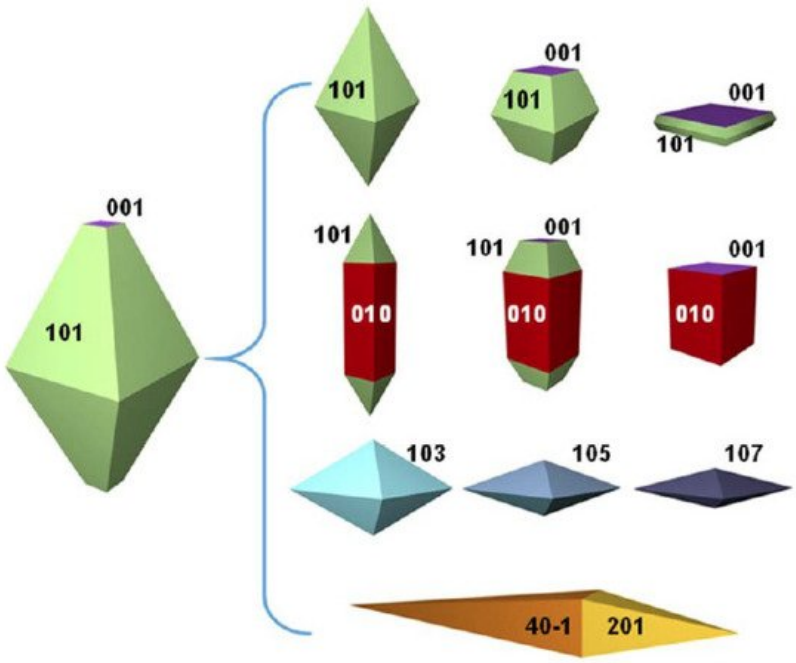

Figure 1. Equilibrium crystal shape of anatase TiO_2 through the Wulff construction and the evolved other shapes. (Reprinted with the permission of ref. [14], copyrights 2014 © American Chemical Society).

Even though the design and morphologically controlled synthesis of TiO 2-001 is considered to be a hot spot in scientific research, it still has some drawbacks like its wide band gap and high recombination rate [24]. These drawbacks can easily be overcome by coupling them with other materials to form TiO 2-001-based composites. For example, doping TiO 2-001 with metal (transition or rare-earth metal) or non-metal ions (C, F, S, N) can make them responsive to visible light [25]. Higher rates of recombination can be suppressed by noble metal deposition on the TiO 2-001 surface [26][27]. When coupled with carbon-based materials, TiO 2-001-based composites show excellent properties, such as high surface area, high absorptivity of dyes and high charge separation [28][29]. These properties make them applicable for many areas of science and technology ranging from adsorption, catalysis and photocatalysis to biomedicine, environmental monitoring and cleanup, energy conversion and storage, etc [30][31]. Hence, it is crucial to highlight the recent progress in the photocatalytic performance of TiO 2-based composites with {001} facets as a future energy material.

This review begins by explaining the role of {001} facets in improving the photocatalytic performance of TiO 2-001 photocatalysts. Then, a brief discussion is given on the modification of the catalysts by doping and coupling mechanisms. Further, we focus on the synthesis routes to obtain TiO 2-001 and modified TiO 2-001-based composites. This is then followed by the various applications of these composites which include environmental remediation by dye degradation, H 2 generation, CO 2 reduction and energy generation through Li-ion batteries. Finally, we present a conclusion and future scope of this emerging field which highlights the major challenges and some invigorating perspectives for future research.

2. Properties of {001} Facets in TiO2

Many researchers have investigated the effect of dissociative adsorption on the photoactivity of TiO 2 crystals. They pointed out that the higher the percentage of {001} facets, the higher the photooxidation reactivity for similarly sized TiO 2 particles.

2.1. Dissociative Adsorption

In a recent study, it was found that the {010} facets could only absorb water molecules on its surface while the {001} facets could dissociate the water molecules, producing hydroxyl and other reactive radicals [32]. It is proposed that the {001} facets could also facilitate transfer of these charge carriers showing higher photocatalytic efficiency [33]. The dissociative adsorption of reactant molecules on {001} facets appears to reduce their activation energy and affect the reaction mechanism at the molecular level in the photocatalytic reaction. Similar chemical activity has also been observed in a wide range of organic species adsorption and other applications such as bacterial inactivation, verifying the unique surface chemistry of the {001} facet [34][35].

2.2. Charge Separation

Besides enhanced dissociative adsorption, charge separation of photogenerated charge carriers can also be mediated by {001} facets [36]. This can be mainly attributed to the unsaturated Ti atoms and defects (oxygen vacancy) present on the surface. The surface of TiO_2-001 nanomaterials exhibits high density of active, five-fold coordinated Ti atoms (Ti5c) and wide Ti-O-Ti bond angles, as can be seen in **Figure 2**a [37]. This gives rise to the generation of a higher number of oxygen vacancies on the surface. Liu et al. proposed that oxygen deficiency within TiO_2-001 induces the specific surface reconstruction in combination with surface chemical species, which facilitates the interfacial electron transfer and e^-/h^+ charge separation [38].

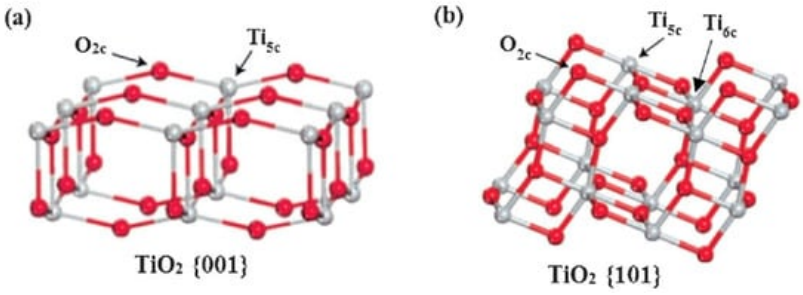

Figure 2. Schematic of surface atomic structure of anatase {001} and {101} crystal facets. (**a**) Large bond angles of Ti-O-Ti on the more reactive {001} surface. (**b**) Narrow bond angles of Ti-O-Ti on the less reactive {101} surface. (Reprinted with the permission of ref. [33], copyrights 2008 © Nature Publishing Group).

2.3. Optical Properties

Apart from preferential oxidation–reduction ability, the band gap of the TiO_2 nanomaterials would also change according to the arrangements of crystal facets on the surface [39]. Based on X-ray photoelectron spectroscopy (XPS) VB spectra and DFT electronic structure calculations, Liu et al. revealed two significant points: (1) the band gap of {001} facets was smaller than that of {101} facets, and (2) the VB maximum of {001} facets was identical to that of {101} facets and thus the CB minimum of {001} facets was lower than that of {101} facets. (**Figure 3**d) [40]. Hence, the UV-Visible spectrum of anatase TiO_2 with 72% {101} facets show blue shifts compared to that with 72% of {001} facets. This electronic band difference would certainly affect the photocatalytic activity of the catalysts in the visible light region [41]. However, up to now, no appreciable visible activity has been observed for pure anatase TiO_2 exposed with {001} facets. To make visible light active, these nanomaterials are coupled with other materials.

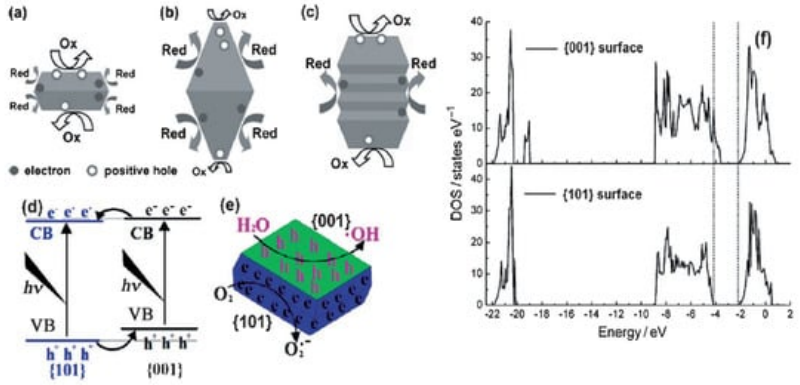

Figure 3. Schematic illustrations of spatial separation of redox sites on the anatase with exposed {001} and {101} crystal facets. (**a**–**c**) Different shapes of TiO_2 particle with a decahedral particle with {001} facets as oxidation sites and {101} facets as reducing sites. (Reprinted with the permission of ref. [42] copyrights 2009 © American Chemical Society). (**d**) Electronic band structures of the {001}{101} facets. (Reprinted with the permission of ref [43] copyrights 2013 © Elsevier). (**e**) Distribution of electrons and holes on the {001} and {101} facets. (**f**) DOS of TiO_2 {001} and {101} surfaces. (Reprinted with the permission of ref. [44], copyrights 2011 © John Wiley and Sons).

2.4. Photocatalytic Selectivity

The selectivity of the photocatalysts towards pollutants/organics is a very important aspect for its conversion/transformation. The selectivity of the TiO_2 can be enhanced by increasing the percentage of {001} facets on its surface. Li et al. demonstrated that the photocatalytic selectivity for the conversion of toluene to benzaldehyde can be

enhanced by increasing the specific surface area of exposed {001} facets. [45]. Similarly, the rate of photoconversion of azo dyes is found to be higher for the TiO_2-001 materials [46].

3. Methods to Modify the Properties of TiO_2-001 Surfaces

3.1 Doping

One of the most common methods to modify the properties of TiO_2-001 is through doping. Doping intentionally introduces impurities into pure TiO_2-001 semiconductors and can be done for the purpose of modulating its physical, chemical and optical properties [47]. The choice of the dopant is dependent upon its properties, such as ionic radii, conductivity and chemical stability. Here, we will discuss metal and non-metal ion doping [48].

3.2 Codoping

Heterostructuring the TiO 2-001 by codoping with two or more dopants is reported to achieve significant synergistic effects compared to their single ion doped or undoped TiO 2 counterparts [49][50]. The strong interaction between these dopants within the TiO 2 matrix alters the charge carrier transfer-recombination dynamics and shifts the band gap absorption to the visible region [51]. In the case of Ni and N [52], N broadens the absorption profile, improving the photoutilization of TiO 2, and generates more electron–hole pairs, while Ni doping restrains the increase of grain growth and leads to crystal expansion, retarding the recombination of charge carriers and thus resulting in the faster degradation of MO compared with single ion doping or undoped TiO 2 under UV light.

3.3 Coupling TiO2-001 with semiconductor

Metal oxides, such as Cu 2O [53], Fe 3O 4 [54], Cds [55], MoO 3 [56], SnO 2 [57], and so on, have been considered for band gap engineering of TiO 2 which are discussed in detail in application section.

4. Synthesis of TiO2-001 and TiO2-001-Based Composites

F-terminated anatase TiO2 surfaces have the lowest γ for both {001} and {101} facets among the 12 non-metal-terminated surfaces, and (2) {001} facets are preferential and more stable compared to {101} facets for F-terminated anatase TiO2 crystals. There is strong preferential interaction between fluorine and the {001} facets of anatase TiO2 crystals which enhances the relative stability of the {001} facets during the crystal growth. Hence, researchers used HF as a capping agent and TiF 4 as raw material in a hydrothermal reaction to synthesize TiO 2-001.

However, F-containing compounds generate toxic and corrosive substances at elevated temperatures in hydrothermal synthesis [58]. Moreover, due to the strong interaction between TiO_2-001 crystal surface and F^- ions, removing them is very difficult. Thus, developing a fluorine-free synthesis methodology is very necessary. To date, there are some papers reporting fluorine-free reagents such as trategies for fabricating anatase TiO_2-001, which are ethylene glycol, H2SO4 and H2O2.

5. Applications

Photocatalytic dye-degradation

Photocatalytic H2 generation

Li-ion batteries

Dye sensitized solar cells

Biomedical applications

Sensing

Drug delivery

6. Conclusions and Future Scope

Intensive research efforts on TiO 2-001-based materials, for their application in environmental remediation and energy conversion, have taken place over the last few years. The continuous advancement in the synthesis methods and modification techniques of TiO 2-001 materials have expanded the capabilities of TiO 2 to include visible light absorption,

suppressed rate of recombination, higher electronic conductivity and higher surface area with more active sites. This expands the possibilities of TiO 2 applications into new and diverse areas. Despite the huge development in theoretical studies and experimental investigations involving TiO 2-001 and their composites, practical applications in this field are still in the preliminary stages and many challenges exist in several aspects. Some of the challenges are listed below.

The photocatalytic properties of TiO 2-001 materials can be amended by the interaction with new materials, which include light harvesters, charge transport materials, additives and interfacial modifiers. Moreover, many efforts must be made to develop large-scale preparation techniques for high-quality modified TiO 2-001 materials i.e., TiO 2-001-based composite materials.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as well as small-angle X-ray/neutron scattering (SANS/SAXS), are the widely used techniques to investigate the morphologies of {001} and {101} faceted anatase TiO 2 nanocrystals. However, these techniques can only provide selected local morphology information. Moreover, these techniques failed to probe the evolution of TiO 2 surface/interface structures in working conditions, which is crucial to study the complex phase transformation and device stability. Hence, more powerful techniques such as near edge X-ray absorption fine structure (NEXAFS) spectroscopy and neutron pair distribution function (PDF) should be used to obtain accurate average morphology and atomistic structures of {001} and {101} faceted anatase TiO 2 nanocrystals. Moreover, in situ characterization techniques must be developed to reveal the photocatalysis reaction process.

Overall, we believe that future research efforts and developments can benefit TiO 2-001 composites as a next generation material for energy conversion and environmental remediation.

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