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Sulfur doped anatase TiO_2 single crystals with a high percentage of {0 0 1} facets

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ABSTRACT

Extending the response range of wide-bandgap (3.2 eV) anatase TiO_2 photocatalysts into the visible light range can play an important role in promoting the practical applications of photocatalysts. Here, we report a route to prepare sulfur doped anatase TiO_2 single crystal sheets with a high percentage of {0 0 1} facets. The resultant TiO_2 sheets were investigated by a combination of experimental characterizations and electronic structure calculations. The synthesized sulfur doped anatase samples show an additional visible light absorption band from 400 nm to ca. 550 nm and some visible-light photocatalytic activity in $^{\cdot}OH$ radical generation and photodecomposition of organic dyes. The Ti–S bond structure causes not only visible light absorption but also changes to an extent the surface structures of doped anatase TiO_2 sheets. Theoretically, localized 3p states of S formed in the bandgap are implicated for the visible light absorption of the sulfur doped anatase TiO_2.

1. Introduction

Since Fujishima and Honda discovered photocatalytic splitting of water on a TiO_2 electrode in 1972 [1], crystalline TiO_2 has attracted a great deal of research interest because of its promising applications such as in photovoltaic cells, photo-/electrochromics, photocatalysis, photonic crystals, self-cleaning coatings, and sensors [2–8]. Among three natural crystal phases (anatase, rutile and brookite) of TiO_2, anatase plays a dominant role in photocatalysis applications due to a generally observed superior photocatalytic efficiency as well as facile synthesis. To further argument the efficiency of anatase TiO_2 for such applications, various morphologies (i.e. rod, tube, sheet, wire, solid/hollow sphere, etc.) have been developed to date via different synthetic strategies. Commonly, titanium (III/IV) halide or alkoxide compounds were used as titanium source [9]. Recently, Yang et al. reported well-faceted anatase titanium dioxide single crystals with a large percentage of reactive {0 0 1} facets by using TiF_4 as a precursor because of its extremely high binding energy of Ti–F and thus relatively low hydrolysis process [10]. Subsequently, increasing attention has focused on the synthesis of anatase TiO_2 sheets with dominant {0 0 1} facets and many interesting results have been achieved [11–16]. In all these cases, anatase TiO_2 sheets will generally have no visible-light response due to the characteristic large bandgap (ca. 3.2 eV) of TiO_2. However, from the view point of utilizing solar light to derive the desired catalysis process, visible-light responsive TiO_2 is crucial. Nonmetal doping of elements such as N [17,18], C [19], S [20], B [21], I [22], F [23], P [24] has shown great potential for introducing visible light absorbing functionalities of TiO_2. However, it has remained a challenge to implement such doping within the morphology-controlling synthetic routes devised to date that can yield anatase TiO_2 sheets with dominant {0 0 1} facets. This is because well-faceted anatase TiO_2 sheets usually have very high crystallinity, making it hard or nearly impossible to incorporate dopants into them by mild post-treatment, while the addition of dopant precursors in the reaction medium can often negatively influence the nucleation and growth of anatase TiO_2 sheets, such that no desirable TiO_2 sheets are obtained [25]. New synthetic strategies directed towards this objective are therefore of great significance.

In recent work [25], we have realized by a new synthetic route the incorporation of nitrogen dopant into anatase TiO_2 sheets with ca. 60% {0 0 1} facets, demonstrating consequent visible light absorption band between 400 and 570 nm as well as visible-light photoactivity. The key strategy in this route is to use crystal compound titanium nitride (TiN) hard to dissolve where both Ti and the N dopant are contained within a single precursor for TiO_2. Capitalizing on this recent step forward, it is expected that such a synthetic route may be extended to prepare other nonmetal doped anatase TiO_2 sheets with preferential {0 0 1} facets by employing corresponding precursors. In this work, this expectation is indeed realized. Sulfur doped anatase TiO_2 sheets with a large percentage of reactive

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{0 0 1} facets have been synthesized from the hydrofluoric acid hydrolysis of crystalline titanium sulfide (TiS_2). These TiO_2 sheets are found to exhibit visible light absorption and corresponding photocatalytic activity, and we explore by a combination of experimental characterization and electronic structure calculations the structural and mechanistic features underlying these advantageous properties. To the best of our knowledge, the work reported herein represents the first incidence of incorporating sulfur dopant into well-faceted anatase TiO_2 sheets with preferential {0 0 1} facets.

2. Materials and methods

2.1. Synthesis procedure of sulfur doped anatase TiO_2 sheets

TiS_2 (Alfar Aesar) was employed as the TiO_2 precursor. In a typical synthesis procedure, TiS_2 powder precursor (varying in concentration between 5 and 20 mM) was suspended into the aqueous solution of 20 mL hydrofluoric acid (HF) (varying in concentration between 20 and 75 mM), followed by hydrothermal treatment in a Teflon-lined autoclave with a volume of 100 mL at 180 °C for 12 h. After reaction, the products were harvested by centrifugation method and washed with deionized water three times to remove dissoluble ionic impurities. Then the samples were vacuum dried under room temperature for 12 h.

2.2. Characterization

X-ray diffraction patterns of samples were recorded on Rigaku diffractometer using Cu irradiation. Morphology and crystal structure was determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) performed on Navo Nano-SEM 430 and Tecnai F30 instruments. Raman spectra were collected on LabRam HR 800. Chemical compositions and valence band spectrum of doped anatase TiO_2 sheets were analyzed using X-ray photoelectron spectroscopy (Thermo Escalab 250, a monochromatic Al Kα X-ray source). All binding energies were referenced to the C 1s peak (284.6 eV) arising from adventitious carbon. The optical absorbance spectra of the samples were recorded in a UV–visible spectrophotometer (JACSCO-550).

2.3. ·OH radical tests

Five milligram of photocatalyst was suspended in 80 mL aqueous solution containing 0.01 M NaOH and 3 mM terephthalic acid. Before exposure to light irradiation, the suspension was stirred in dark for 30 min. Then 5 mL of the solution was taken out after each desirable time, and centrifuged for fluorescence spectrum measurements. During the photoreactions, no oxygen was bubbled into suspension. A fluorescence spectrophotometer (Hitachi, F-4500) was used to measure the fluorescence signal of the 2-hydroxy terephthalic acid generated. The excitation light employed in recording fluorescence spectra was 320 nm. The light source was a 300 W Xe lamp (Beijing Trusttech Co. Ltd., PLS-SXE-300UV) with the wavelength of 220–770 and 420–770 nm.

2.4. Photodegradation of Rhodamine B tests

The photodegradation tests were carried out by adding 50 mg of TiO_2 sample into 100 mL of 2×10^{-5} mol L^{-1} Rhodamine B solution. The suspension was stirred in dark for 30 min to ensure the saturated adsorption of Rhodamine B before illumination. Then 5 mL of the solution was taken out every 30 min, and centrifuged for subsequent measurements. The concentration of Rhodamine B solution was determined with a UV–visible spectrophotometer by monitoring the optical density of Rhodamine B at 554 nm. The light source used for the photodegradation is the same as that for the generation of OH radicals above.

2.5. Computational methods

To investigate the doping effect at the electronic level, the geometric and electronic structures of S-doped anatase TiO_2 with were studied in the framework of density functional theory (DFT) within the generalized-gradient approximation (GGA) [26]. Anatase TiO_2 surfaces are represented by the majority (1 0 1) and the minority (0 0 1), described by 4×4 slab models with 15–18 atomic layers, as shown in Fig. 5. Based on our tests, TiO_2 surfaces can be described very well with such slab models in terms of total energies of TiO_2 substrates and adsorption energies of sulfur atoms. Spin-polarized calculations were carried out using the exchange–correlation functional of Perdew–Burke–Ernzerhof (PBE) [27,28], based on the numerical double-numerical polarization (DNP) basis set, which has been implemented in the Dmol3 modules [29,30]. The above computational approach has been successfully employed in our previous studies of N-, I- and B/N-doped TiO_2 structures [31–34]. More tests and the discussion regarding the efficiency and reliability of the numerical basis set can be found in Delley's work, in which the estimated errors from the PBE functional with the DNP basis set were supposed to be lower than those with the hybrid B3LYP/6–31G** functional [31]. During our calculations, the convergence criteria for structure optimizations were set to: (1) energy tolerance of 1.0×10^{-6} Ha per atom, (2) maximum force tolerance of 1.0×10^{-3} Ha/Å and (3) maximum displacement tolerance of 1.0×10^{-3} Å. The energy tolerance for self-consistent field iterations for structural optimizations and electronic calculations are set as 5.0×10^{-6} Ha and 1.0×10^{-6} Ha, respectively. Considering the large size of our slab models, the *k*-space is sampled by gamma point only, but larger sets of *k* points have been tested and no significant changes in the calculated results are found.

3. Results and discussion

Fig. 1 illustrates the X-ray diffraction (XRD) patterns of original crystalline TiS_2 and the as-prepared TiO_2. The starting solid TiS_2 in dark-green colour crystallizes in a layered structure by stacking the layers of TiS_2 via the relatively weak Van-der Waals forces [35]. The diffraction intensity of TiS_2 shown in Fig. 1a is very similar to the bulk TiB_2 crystals (JCPDS No. 65-3369) [35], enclosed mainly by thermodynamically stable facets such as {0 0 1} and {1 0 1}. By treating TiS_2 (9 mM) in HF solution (50 mM) under 180 °C for 12 h, TiO_2 in pure anatase phase (space group $I4_1/amd$) [10] was synthe-

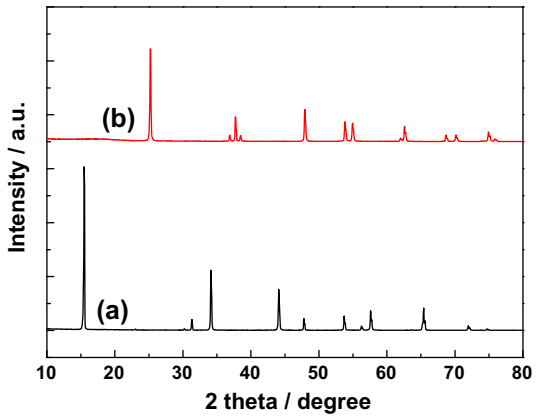

Fig. 1. XRD patterns of pristine TiS_2 (a) and sulfur doped anatase TiO_2 (b) synthesized.