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Synthesis of nitrogen doped faceted titanium dioxide in pure brookite phase with enhanced visible light photoactivity

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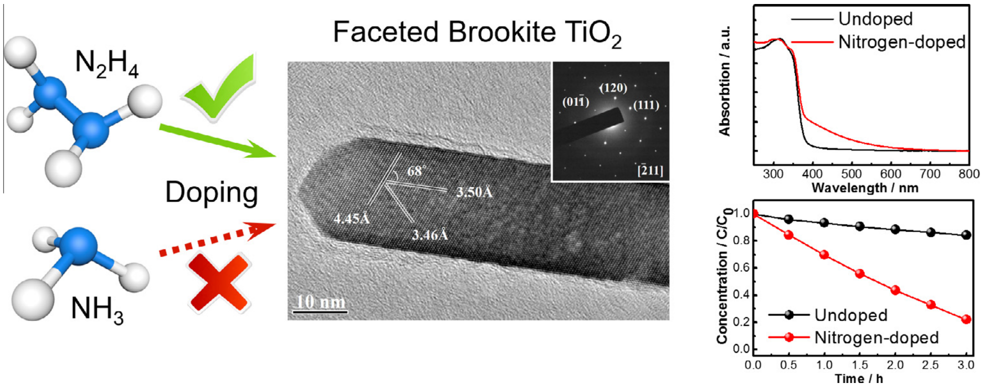
GRAPHICAL ABSTRACT



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ABSTRACT

Brookite titanium dioxide (TiO_2) is rarely studied, as compared with anatase and rutile phases TiO_2, due to its comparatively lower photoactivity. It has been recently reported that brookite TiO_2 with active facets exhibits excellent performance, however, synthesis of such faceted brookite TiO_2 is difficult because of its low thermodynamic phase stability and low structural symmetric. Furthermore, like faceted anatase and rutile TiO_2, faceted brookite TiO_2 is not responsive to visible light due to its wide bandgap. In this study, a novel dopant, hydrazine, was introduced in the development of nitrogen doping. By applying this dopant, nitrogen doped brookite nanorods with active {120}, {111} and {01$\bar{1}$} facets were successfully synthesized. The resultant materials exhibited remarkably enhanced visible-light photoactivity in photodegradation.

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1. Introduction

Titanium dioxide has been the most intensively investigated binary transition metal oxide in the past four decades. It exists mainly in three nature phases, including anatase, rutile and brookite. Compared with anatase and rutile, brookite is the least investigated phase, due to the essential difficulty in its synthesis and its comparatively lower photoactivity [1]. In recent years, several studies have been reported on high-quality pure brookite TiO_2 nanotubes [2], nanosphere [3,4], nanorods [5–7], nanoflowers [8,9] and nanosheets [10,11], some of which showed excellent photoactivities. The synthetic TiO_2 crystals enclosed by clear facets, particularly high-energy facets were hardly found [12], until the breakthrough in the synthesis of high quality anatase crystals with a high percentage of reactive high-energy {001} facets was made

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by Yang et al. [13]. As the development of faceted anatase and rutile TiO_2 has received increasing attention, brookite TiO_2 with active facets has also been produced [14]. For instance, Lin et al. prepared brookite TiO_2 nanosheets with active {2 1 0}, {1 0 1}, and {2 0 1} facets exhibited remarkable photocatalytic activity in contrast to nanoparticles with irregular facets [11]. This result changed the conventional thought that brookite TiO_2 had lower photoactivity. Though great progress has been made in the research of brookite, so far there is no literature reporting the visible light photocatalytic activity of pure faceted brookite TiO_2, due to its large band gap (>3.0 eV). From the viewpoint of optimizing solar energy conversion, it is highly desired to introduce visible-light photoactivity into brookite TiO_2 catalysts [15].

Comparing with numerous reports on nitrogen doped anatase and rutile TiO_2 [16], the studies of brookite TiO_2 doping were rare. Although there are some studies on non-metal doped anatase/brookite [17], or anatase/rutile/brookite [18,19] TiO_2 polymorphs, it is difficult to identify the contribution of brookite toward visible-light photoactivity in such multi-polymorph systems. Furthermore, in these studies, the morphology control, which plays a crucial role in enhancing the photoactivity of catalysts [16,20–23], has been overlooked. In the synthesis of doped brookite with active facets, a strict morphology control is essential yet considerably challenging. The difficulties, we believe, mainly lies in two aspects: (i) The reaction condition of preparing pure brookite TiO_2 is essential. Because the calorimetric data for the transformation enthalpies of anatase to rutile, and of brookite to rutile suggests the thermodynamic phase stability should be in the order rutile > brookite > anatase [24]. Utilizing improper dopant precursors and/or facet capping agents would easily change the chemical environment, leading to other or mixed phases; (ii) In comparison with anatase (tetragonal, $I4_1/amd$) and rutile (tetragonal, $P4_2/mnm$), brookite (orthorhombic, $Pbca$) has a low structural symmetry [25]. The addition of dopants tends to have adverse effects on the low-symmetric precursors, which could consequently affect the atomic structure of brookite crystals and the formation of active facets. Therefore, finding a proper dopant is a key for the successful development of faceted brookite with enhanced photoactivity by doping.

In this study, nitrogen doped pure brookite TiO_2 nanorods with active facets were prepared via a simple hydrothermal approach. Hydrazine (N_2H_4) was introduced in the synthesis as a nitrogen dopant, and titanium bia (ammonium lactate) dihydroxide (TALH) was used as the titania precursor. Such N-doped brookite TiO_2 nanorods with active {1 2 0}, {1 1 1} and {0 1 1} facets showed remarkably enhanced visible light photoactivity in the photodegradation of Rhodamine B (RhB).

2. Experimental section

2.1. Preparation of brookite TiO_2 nanorods

As-received 5 mL of TALH solution (50% Sigma–Aldrich) was dropped into 30 mL 6 M urea aqueous solution. Then, the solution was transferred into a Teflon-lined stainless steel autoclave. The autoclave was kept at 200 °C for 18 h in the oven. After reaction, the products were collected by centrifugation and washed with deionized water for 5 times to remove the ionic impurities, and then dried at 80 °C in air.

2.2. Preparation of N doped brookite TiO_2 nanorods

As-received 5 mL of TALH solution was dropped into 30 mL 3 M urea aqueous solution. Later, the desired amount (1–4 mL) of hydrazine monohydrate (N_2H_4, 64–65%, Sigma–Aldrich) was dripped into the mixture under stirring. Then, the solution was transferred into a Teflon-lined stainless steel autoclave. The autoclave was kept at 200 °C for 18 h in the oven. After reaction, the products were collected by centrifugation and washed with deionized water for 5 times to remove the ionic impurities, and then dried at 80 °C in air. The as-prepared powder was yellow in color and was denoted as NB-X (here X represents X mL of hydrazine monohydrate used for synthesis).

2.3. Characterization

X-ray diffraction patterns of the samples were recorded on a Rigaku diffractometer using Cu Kα irradiation. Morphology was determined using transmission electron microscopy (TEM, JEOL 1010 and 2100). The Brunauer–Emmett–Teller (BET) surface area was determined by nitrogen adsorption–desorption isotherm measurements at 77 K (ASAP 2010). Chemical compositions and valence band spectra of TiO_2 were analyzed using X-ray photoelectron spectroscopy (XPS) (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 by a UV–visible spectrophotometer (JACSCO-V650).

2.4. Photoactivity analysis

The photocatalytic experiments were carried out by adding 50 mg of different samples into 100 mL of 2×10^{-5} M Rhodamine B (RhB) solution. The suspension was stirred in dark for 30 min to obtain the saturated adsorption of RhB before illumination. The light source used was an AM 1.5 solar simulator (Oriel) equipped with a 150 W xenon light source and an AM-1.5G type filter (Newport, 81094). The light intensity of the solar simulator was adjusted by using an optical power meter (Newport, 1918-c) with a detector (818P-040-25). A long-pass glass filter with 420 nm was employed to evaluate the photocatalytic activity in visible light range.

3. Results and discussion

3.1. Phase and microstructure of nitrogen-doped brookite TiO_2

Fig. 1 shows the UV–visible absorption and XPS spectra of undoped and doped brookite TiO_2 samples. As shown in Fig. 1a, undoped brookite TiO_2 has the pristine absorption edge at 376 nm. NB-1 has a visible-light absorption shoulder comparing with undoped brookite. As the amount of N_2H_4 was increased, other samples (NB-2, NB-3 and NB-4) exhibited enhanced visible-light response. The visible-light absorption shoulder indicates that some localized states in the bandgap of brookite TiO_2 are responsible for the visible light absorption.

The chemical states of the nitrogen dopant were investigated by XPS. It can be seen in Fig. 1b that the binding energy of N 1s in brookite TiO_2 is ~400 eV, which is associated with the O–Ti–N structure [15,17]. As the amount of N_2H_4 increases, the intensity of the signal of N 1s is enhanced. Meanwhile, the binding energy of Ti 2p and O 1s accordingly shifts from 458.7 eV and 530.0 eV to 458.4 eV and 529.7 eV, respectively (Fig. 1c and d). The results suggest that the visible light absorption upon doping is attributed to the localized states of N 2p in the bandgap of TiO_2.

The morphology of undoped brookite TiO_2, NB-1, NB-2, NB-3 and NB-4 was revealed by transmission electron microscopy (TEM) and the results are shown in Fig. 2. The undoped brookite TiO_2, NB-1, NB-2 and NB-3 have similar rod shape with ~100 nm

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