Highly stable visible-light photocatalytic properties of black rutile TiO₂ hydrogenated in ultrafast flow

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Abstract

The hydrogenation and introducing oxygen vacancies (V_O) can lead to surface lattice-disorder in TiO_2 , which is a new form of TiO_2 named black TiO_2 , with excellent visible-light photocatalytic activity, but this TiO_2 is easy to failure because oxidation makes the concentration of surface V_O decrease rapidly in a short time. In this work, black TiO_2 nanoparticles with V_O almost concentrated inside nanoparticles were fabricated under ultrafast hydrogen flow. These bulk V_O shortened the bandgaps of black TiO_2 , enhanced its visible light absorption, and meanwhile provided extremely strong stability. A series of characterization methods confirmed the location of V_O , and degradation experiments on Cr^{6+} or rhodamine B demonstrated the good visible-light photocatalytic performance of our material. After 18 months of natural aging treatment (in the air), our samples showed no discoloration and maintained 89.5% photocatalytic efficiency, and further study exhibited that this black TiO_2 also contained excellent acid-resistance and moderate alkaline-resistance. This work could help design lattice-disorder to obtain more stable and practical black TiO_2 .

1. Introduction

TiO_2 has been widely studied in dealing with environmental and energy problems since its photocatalytic property of decomposing water was discovered in 1972 [1–3]. However, naturally occurring TiO_2 can only be excited by ultraviolet to generate electron-hole pairs owing to its wide bandgap and weak visible-light absorbance [4, 5]; this limitation makes TiO_2 a long distance to practical application. Doping [6, 7], compounding with other semiconductor oxides [8], such methods have been tried for narrowing the bandgap of TiO_2 and enhancing its visible-light photocatalytic performance.

In 2011, Chen et al. reported a material called "black TiO_2 " with an amazing narrowed bandgap (1.54 eV) and significantly improved visible-light photocatalytic activities compared to white TiO_2 [9], quickly attracting public eyes. These TiO_2 nanoparticles changed from white to black after being reduced in a hydrogen atmosphere with high pressure, but their phase kept TiO_2 . This form of TiO_2 had significant absorption of visible light, and in subsequent reports TiO_2 with a similar mechanism but slightly lighter color was also called black TiO_2 [10, 11]. Although many methods for the preparation of black TiO_2 have been developed [12–14], hydrogenation remains the most used method for the reason of high-efficiency and ease of industrial production. Extensive efforts had been done on the formation mechanism of black TiO_2 [13, 15–17], while the most generally accepted explanation was that oxygen vacancies (V_O) played a leading role in forming black TiO_2 . V_O could change band structures and visible-light absorbance of black TiO_2 via introducing donor energy levels in conduction bands [9, 17–19]. The generation of V_O was often considered to be accompanied by the appearance of Ti^{3+} [20, 21], and they could both promote the separation of photogenerated electron-hole pairs. Other defects such as surface hydroxyl groups had also been reported to be responsible for the formation of black TiO_2 with its excellent visible-light photocatalytic performance. Moreover, these crystal defects often accumulated on the material surface,

resulting in surface disorder and thus typical amorphous shells could be usually observed on the surface of black TiO₂.

Although the ability of black TiO₂ to utilize visible light had been dramatically improved, the surface defects were easy to be oxidized, leading to a degradation concentration of defects so black TiO₂ were instable, serious constraining to its further application [22, 23]. Some researchers began to concern and solve this problem, while the photocatalytic performance of black TiO₂ long treated under various external risk factors (O₂, H⁺, OH⁻, etc.) was still not investigated. For example, Lan et al. adopted an in-situ reduction method to form Ti³⁺ as much as possible inside the material to stabilize black TiO₂ [23]. At the same time, one study revealed that there are two types of V_O and they may correspond to different locations [24].

Herein, black rutile TiO₂ nanoparticles with stable visible-light photocatalytic activity were prepared through hydrogen in an ultrafast flow. A series of temperature gradient experiments were carried out to found an optimal parameter and the samples hydrogenated at 800°C contained the best photocatalytic properties. Various characterization methods revealed good surface crystallization but a mass generation of V_O in the body of black TiO₂, and the high concentration of internal defects rather than surface defects was believed to an important cause of stabilizing black TiO₂. The natural aging process of 18 months indicated 3 times longer shelf life of our samples than traditional black TiO₂, besides, an acid-alkali resistance experiment further investigating the stability of black TiO₂.

2. Experiment

2.1 materials

White rutile TiO₂ (50 nm in diameter, provided by Ansteel Research Institute of Vanadium and Titanium) was heated in nitrogen flow inside a furnace with a 10°C/min heating rate firstly. After the furnace temperature reached 150°C, nitrogen was replaced with ultrafast pure hydrogen flow (99.9%, 1.2 L/min), and then they were held at different temperatures (700–900°C) for 1h. Black TiO₂ was obtained after the samples cooled to room temperature. In the following, black TiO₂ hydrogenated at different temperatures was abbreviated to 700°C-H-TiO₂, 750°C-H-TiO₂, etc.

2.2 photocatalytic test

4 μmol/L Rhodamine B (RhB, provided by ChengDu Chron Chemicals Co.,Ltd) aqueous solutions were the reaction substrate of most photocatalytic experiments. In each experiment, 10 mg TiO₂ nanoparticles were dispersed into a 250 mL RhB solution. After the mixture reached an adsorption-elution balance in the dark, visible-light photocatalytic experiments were carried out under a xenon lamp whose ultraviolet light had been cut. 5 mL mixture was taken for filtration and centrifugation each time, and then the

absorbance of supernatants was measured to determine the concentration of RhB. The parameters of stability experiments under different environments would be described later in this article.

2.3 Characterization

The colors of black TiO₂ gradually deepened with hydrogenation temperature increasing, which matched with the ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS, measured on Shimadzu UV-3600). The phase analysis was obtained by an X-ray diffraction spectrometer (XRD, Rigaku smartlab9) with Cu K α X-ray. Electron paramagnetic resonance (EPR) was carried out at 77 K on a Bruker ELEXSYS-II E500 spectrometer. The information about surface hydroxyls and Ti states were obtained by an X-ray photoelectron spectrometer (XPS, Thermo Fisher Scientific K-Alpha). Microphotographs of materials were obtained by scanning electron microscopy (SEM, FEI Inspect F50) and transmission electron microscopy (TEM, FEI Tecnai G2 F20).

3. Results And Discussion

Fig. 1 illustrated the XRD patterns (normalization based on the intensity of diffraction peak (110)) of different TiO₂. The main phase of samples hydrogenated at different temperatures all maintained rutile TiO₂, and no obvious change was observed among 700°C-H-TiO₂, 750°C-H-TiO₂, 800°C-H-TiO₂, and white TiO₂. Higher hydrogenation temperatures led to the formation of suboxide titanium, reflecting as tiny splits in the main diffraction peak (27.4°), and a reconstruction process induced by titanium suboxides during reduction processes brought other effects which were detailed discussed in supporting information [25, 26].

The information about appearance, absorbance, and bandgaps of different TiO₂ was given in Fig. 2. According to Fig. 2a, the colors of black TiO₂ were gradually darkened as hydrogenation temperatures went up. The deepening of colors brought photocatalysis marked significance that visible light could not be absorbed by white TiO₂ but black TiO₂ broke through this limitation. The UV-Vis DRS showed in Fig. 2b exhibited a similar result that the visible-light absorbance of white TiO₂ was almost 0, while black TiO₂ had significantly stronger absorbance proportional to hydrogenation temperatures. The values of bandgaps shown in Fig. 2c were obtained by mathematical processing Fig. 2b and the following equation:

$$\alpha h\nu = A(h\nu - E_g)^2. \quad (1)$$

Here, α , ν , and E_g represented absorption coefficient, frequency, and bandgaps respectively. This formula was the main calculation method of black TiO₂ bandgap and was widely used by researchers [27,28]. The bandgap of white TiO₂ (rutile) in our experiments was 2.94 eV which was closed to experienced data 3.0 eV, while black TiO₂ had constantly narrowing bandgaps with hydrogenation temperatures raising. 800°C-H-TiO₂ had a markedly narrowed bandgap of 2.71 eV, and furtherly the bandgap of 900°C-H-TiO₂

was down to 2.05 eV. These characteristics indicated that white TiO₂ nanoparticles were successfully transformed to black TiO₂.

Fig. 3 presented the micromorphology information of black TiO₂ hydrogenated under different temperatures. White TiO₂ nanoparticles without treatment were in the shape of spindles with a length-diameter of nearly 50 nm, while black TiO₂ nanoparticles were ellipsoidal in obvious sphericity due to the thermal effect in annealing processes, and the size of nanoparticles also slightly increases continuously with annealing temperature raising. In this paper, the nanoparticle sizes of different black TiO₂ were mostly between 70-110 nm, so the interference of large particle size on photocatalytic performance could be eliminated. The lattice-disordered shell was a significant feature of traditional black TiO₂, which was interestingly not observed in our hydrogenated materials. Lattice stripes at the edge of black TiO₂ nanoparticles were still clear, indicating quite low surface disorder and defect concentration. White TiO₂ had an interplanar spacing of 0.319 nm in (110) face, while this parameter in black TiO₂ expanded to 0.342 nm. This 7.2% expansion was due to the existence of V_O enriched in the body of black TiO₂, and subsequent analysis of crystal defects further verified this conclusion.

The photocatalytic activity of different TiO₂ was determined by the time-depend residual of RhB, as shown in Fig. 4. RhB itself did not degrade under visible light, so its concentration change was caused by the photocatalytic effect of black TiO₂. When the different mixtures of TiO₂ powders and RhB water solution had just been exposed to light, their absorption-dissociation balance reached in the dark would be disturbed, causing an abnormal upward change in the C/C₀ curve of RhB in the first 20 min and this phenomenon disappeared with time growth. As expected, white TiO₂ had no visible-light photocatalytic activity due to its poor ability in utilizing visible light, while black TiO₂ had obvious enhanced photocatalytic activity driven by visible light, further suggesting that black rutile TiO₂ were successfully prepared. RhB degradation rates of black TiO₂ increased with hydrogenation temperatures and visible-light absorbance before 800°C, but an abnormal phenomenon of sharply decreased photocatalytic activity was observed in the experiments of 850°C-H-TiO₂ and 900°C-H-TiO₂, although they had darker colors and narrower bandgaps. This anomaly could be attributed to the changes in crystal planes of different black TiO₂ and the difference in photocatalysis induced by crystal planes [29,30]. This would be detailly discussed in supplemental information. In general, 800°C-H-TiO₂ had the best performance that it could degrade more than 70% RhB in 2 hours, and we also chose another substrate Cr⁶⁺ that was more difficult to decompose to further illustrate the excellent photocatalytic activity of our material, which was revealed in Fig S1.

800°C-H-TiO₂ was selected for more tests and a series of stability experiments because of its optimal performance, and we adopted EPR measurement to reveal the changes from white TiO₂ to black TiO₂ from the angle of lattice defects. As shown in Fig. 4a, for 800°C-H-TiO₂, a small peak at g=2.005 indicated the generation of a small number of V_O [24,31], while the spectrum of white TiO₂ with few crystal defects appeared horizontal. This result explained the variation in bandgaps and absorbance from

white TiO₂ to 800°C-H-TiO₂. V_O produced donor levels under the conduction band [17] and then extended the bottom of the conduction band downward, thereby narrowing bandgaps of black TiO₂. It was worth noting that different V_O peaks correspond to diverse positions of existence, and black TiO₂ reported previously usually had the peaks at both nearly g=1.98 (in the surface and in coexistence with Ti³⁺) and nearly g=2.005 (in the body) [24], while the peak at g=1.98 in 800°C-H-TiO₂ in this paper seemed not obvious. This analysis meant that in 800°C-H-TiO₂ V_O was concentrated mainly inside nanoparticles. According to Fig. 5b, the double peaks at 458.7 eV and 464.5 eV in white TiO₂ could be all assigned to Ti⁴⁺ [14]; the spectrum of 800°C-H-TiO₂ showed a similar result that the total peak was almost identical to the Ti⁴⁺, also indicating that defects Ti³⁺ barely existed in the surface of black TiO₂ nanoparticles. Fig. S2 further illustrated that only a few surface defects existed in our material, and those characteristics may contribute to the excellent stability of 800°C-H-TiO₂.

VB-XPS spectra shown in Fig. 5c gave the levels of valance bands (VB) in different TiO₂. For white TiO₂, the maximum of VB (VBM) was at about 2.65 eV toward the vacuum level, and 800°C-H-TiO₂ had a similar VBM of 2.63 eV. The improvement effect of V_O on black TiO₂ was mainly through introducing donor levels in its conduction band (CB), so their valence band (VB) did not change significantly. The position of CB could be obtained by combining bandgaps with VB. The minimum of CB in white TiO₂ was at -0.29 eV, while that of 800°C-H-TiO₂ was extended to -0.08 eV. This change coincided with the generating of donor levels in the edge of CB, so the bandgaps of black TiO₂ were narrowed and the excitation driven by visible light was also promoted.

Fig. 6 gave the appearance and photocatalytic activity of 800°C-H-TiO₂ after natural aging treatment for 18 months in the air atmosphere. As shown in Fig 6a, 800°C-H-TiO₂ after 18 months of aging treatment still retained a typical appearance of black TiO₂, with no significant difference from initial samples. Fig 6b showed the comparison of photocatalytic performance of 800°C-H-TiO₂ before and after aging treatment. 800°C-H-TiO₂ after aging treatment could degrade 65.3% RhB in 2 h, and its photocatalytic activity was only 10.5% lower than that of the samples before aging treatment, indicating that our black TiO₂ contains great stability and were only slightly oxidized after long-term storage in air. Corresponding to our works, black TiO₂ mainly depending on surface V_O experienced a similar degree of photocatalytic performance attenuation in only 6 months [22]. The circulation experiment result of 800°C-H-TiO₂ after aging treatment was shown in Fig. 6c. Residual efficiency was calculated by the following equation:

$$\text{Residual efficiency} = (1 - C_y / C_{0y}) / (1 - C_x / C_{0x}). \quad (2)$$

The suspension (include the part which was used to measure absorbance) during catalytic experiments was all collected, after that, black TiO₂ powder was filtered from the suspension, cleaned in ultrasonic, and dried in argon. RhB concentration was correspondingly reduced in each subsequent cycle experiment due to the slight quality loss of catalyst, while other experimental parameters of photocatalysis were the

same as those of Fig. 3. The photocatalytic activity of 800°C-H-TiO₂ during 5 cycles of experiments did not change significantly, which further demonstrated its good storability.

To highlight the effect of pH on the material itself, the black TiO₂ powders were pretreated with acid-base instead of directly being put into reaction solutions with different pH as commonly used. Aqueous solutions with different pH were regulated by HCl or NaOH, and then the 800°C-H-TiO₂ powder after 18 months of aging treatment was dispersed in different water for 180 h, respectively. The parameters of subsequent processes were the same as above, and relevant results were shown in Fig. 7. Long-term immersion in acid solution did not decrease the photocatalytic activity of black TiO₂, even that the photocatalytic activity of black TiO₂ was improved due to changes in surface states driven by protonation [32]. A large number of H⁺ interacted with black TiO₂ for a long time, which might improve the absorption capacity of materials to RhB and thus increased their photocatalytic activity. The alkali group gave results of slightly reduced photocatalytic properties of black TiO₂ after being placed in alkali solutions for a long time. In the group of pH=8, 800°C-H-TiO₂ remained 91.4% photocatalytic activity after 180 h treatment, and 800°C-H-TiO₂ had nearly 80% residual efficiency after being immersed for 180 h at a stronger alkali solution of pH=10 or 12. The logarithmic diagram in Fig. 7c showed that the photocatalytic reactions of black TiO₂ before and after treatment were all first-order reactions. In conclusion, our black TiO₂ had excellent acid resistance, while when they were long-term used in alkali water, a little risk of performance decrease may be concerned.

4. Conclusions

In summary, black rutile TiO₂ with extremely stable visible-light photocatalytic performance was effectively prepared in this work. 800°C-H-TiO₂ had the best photocatalytic activity and the high concentration of bulk V_O may be responsible for its enhanced visible-light photocatalytic activity and stability. The stability experiment for 800°C-H-TiO₂ illustrated that our black TiO₂ could maintain photocatalytic activity for 18 months, and also could be stably used in acidic water.

Declarations

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Conflicts of interest/Competing interests

There is no conflict of interest or competing interests to declare that are relevant to the content of this article.

Availability of data and material

The source of the chemical, the process of the experiment, the handling of the data, etc., are transparent.

Code availability

The software application used in this work was also available on other computers.

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Figures

Figure 1

XRD spectra of white TiO_2 and black TiO_2 fabricated by hydrogenating at different temperatures

Figure 2

a Optical images of white TiO_2 and black TiO_2 fabricated by hydrogenating at different temperatures, b UV-Vis DRS spectra of white TiO_2 and different black TiO_2 , c Mathematical processing data of b, d Bandgaps varied with hydrogenation temperature

Figure 3

SEM images of a white TiO₂, b 700°C-H-TiO₂, c 750°C-H-TiO₂, d 800°C-H-TiO₂, e 850°C-H-TiO₂, and f 900°C-H-TiO₂, HRTEM images of g white TiO₂ and h 800°C-H-TiO₂

Figure 4

a Time-dependent RhB residual in visible-light photocatalytic reactions of black TiO_2 fabricated by hydrogenating at different temperatures and white TiO_2 , b The degradation rate of RhB at the end of photocatalytic reaction of black TiO_2 fabricated by hydrogenating at different temperatures

Figure 5

a EPR spectra and b XPS spectra (Ti 2p) of white TiO_2 and $800^\circ\text{C-H-TiO}_2$, c VB-XPS spectra of white TiO_2 and $800^\circ\text{C-H-TiO}_2$, d Bandgap schematic of white TiO_2 and $800^\circ\text{C-H-TiO}_2$

Figure 6

a Optical images of 800°C-H-TiO₂ before and after 18 months of aging treatment, b RhB residual in visible-light photocatalytic reactions of 800°C-H-TiO₂ (before and after 18 months of aging treatment), c RhB residual efficiency in cycle visible-light photocatalytic reactions of 800°C-H-TiO₂ after 18 months of aging treatment

Figure 7

a RhB residual efficiency in visible-light photocatalytic reactions of 800°C-H-TiO₂ which had been pretreated in various pH conditions 180 h (all black TiO₂ were after 18 months of aging treatment, b C/C_0 -T curve of part experiments in a, c Logarithmic processing results of b

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