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Article

One-pot topotactic synthesis of Ti^{3+} self-doped 3D TiO_2 hollow nanoboxes with enhanced visible light response

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ABSTRACT

Ti^{3+} self-doped anatase three-dimensional (3D) TiO_2 hollow nanoboxes were synthesized via a topological transformation process involving template participation by a facile one-pot hydrothermal treatment with an ethanol solution of zinc powder and TiOF_2 . It is worth noting that the 3D TiO_2 hollow nanoboxes are assembled from six single-crystal nanosheets and have dominant exposure of the {001} facets. It is found from EPR spectra that adding zinc powder is an environment-friendly and effective strategy to introduce Ti^{3+} and oxygen vacancy (O_v) into the bulk of 3D hollow nanoboxes rather than the surface, which is responsible for their enhanced visible photocatalytic properties. The photocatalytic activity was evaluated by measuring the formation rate of hydroxide free radicals using 7-hydroxycoumarin as a probe. The sample prepared with zinc/ TiOF_2 mass ratio of 0.25 exhibited the highest RhB photodegradation activity under visible-light irradiation with a degradation rate of 96%, which is 4.0-times higher than that of pure TiO_2 . The results suggest a novel approach to construct *in-situ* 3D hierarchical TiO_2 hollow nanoboxes doped with Ti^{3+} and O_v without introducing any impurity elements for superior visible-light photocatalytic activity.

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1. Introduction

Due to its excellent application in solving the energy crisis and environmental pollution, anatase TiO_2 has attracted much attention for its chemical stability, low toxicity, photo oxidation properties, and environmental friendliness [1]. However, anatase TiO_2 is not a suitable candidate for practical applications due to its large energy gap and rapid recombination of photo-generated electron-hole pairs [2–6]. Therefore, developing a simple method to overcome the 3.2-eV band gap and expand

the absorption edge of titanium dioxide to the visible light range should be studied further [7].

An effective solution to this challenge is to dope the surface or bulk of TiO_2 by modifying or co-doping with different metal or non-metallic ions [8,9]. Metallic or non-metallic elements, such as Cu^{2+} , Fe^{3+} , N and S, act as electron acceptors or donors in the forbidden band of the photocatalyst and induce obvious absorption in the visible light range [10,11]. However, the introduction of other impurity elements may permit hazardous dopants to enter the environment. Other impurity elements

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may cause thermal instability, doping induced charge recombination, requires expensive ion implantation equipment, and generates more carrier recombination centers. Therefore, it will greatly hinder the photocatalytic activity of titanium dioxide and critically restrain its actual application [12].

Ti³⁺ self-doping is a desirable doping modification method which does not require other metal or non-metallic ion impurities and effectively maintains the structure and morphology of TiO₂. The formation of Ti³⁺ or O_v is an effective and environmental-friendly strategy for improving visible light absorption [13]. Until now, only a few methods have been capable of producing Ti³⁺ and O_v-doped TiO₂ nanosheets. Nonetheless, there is still no effective approach for synthesizing Ti³⁺ self-doped three-dimensional (3D) TiO₂ hollow nanomaterials. For example, Si et al. [14] used a simple solution reaction to prepare reduced TiO₂ nanosheets with high energy facets. However, controlling the O_v concentration is difficult, and Ti³⁺ ions are introduced into the surface rather than the bulk of the catalyst. This could significantly inhibit its practical application in different visible light systems. At the same time, these methods are limited because of their high cost, complex processing techniques, and small production scale. Although the preparation and photocatalytic activity of reduced TiO₂ nanomaterials have aroused great interest, research on Ti³⁺ self-doping is far from satisfactory, and there are still many problems left to be resolved in this research area, especially regarding preparation of 3D TiO₂ materials with hollow structure [15].

The phase structure and crystal facets play an important role in TiO₂ catalysts. In recent years, various 3D TiO₂ structures with hollow morphology have been synthesized by various methods, such as TiO₂ tubular structures or hollow spheres constructed from nanorods, nanowires, nanosheets or nanoparticles. However, these three-dimensional structures are primarily based on spherical morphology, which consist of randomly assembled building blocks. The preparation of non-spherical 3D TiO₂ hollow nanomaterials composed of an ordered superstructure or hierarchical structure, such as boxes, remains a major challenge. The relationship between the catalytic properties and high-energy {001} facets has recently attracted an explosion of interest [16]. Both theoretical and experimental analyses have demonstrated that the high energy {001} facets enable efficient separation and transfer of photo-generated electron-hole pairs, and uncoordinated Ti_{5c} atoms in the exposed {001} facets can effectively narrow the energy gap of the catalyst [17]. 3D TiO₂ hollow nanoboxes were fabricated by a topotactic transformation from TiOF₂ precursors [18,19]. In terms of morphology and facet modification, building 3D hierarchical TiO₂ hollow nanoboxes enclosed by six ordered TiO₂ nanosheets with dominant {001} facet exposure to enhance visible light absorption, especially in the originally crystal growth process, is still a difficult problem and is restricted by the critical crystal growth environment. Thus, there is an urgent need to develop a facile and one-pot topotactic synthetic strategy to prepare Ti³⁺ self-doped TiO₂ with 3D hollow structures to enhance the visible light response. To the best of our knowledge, the fabrication of Ti³⁺-doped 3D TiO₂ hollow nanoboxes with exposed {001} facets in the presence of a re-

ductant through a topotactic transformation process with a TiOF₂ template has not been reported.

Herein, we employ a simple one-pot topotactic hydrothermal method to introduce Ti³⁺ and oxygen vacancies into 3D TiO₂ hollow nanoboxes without any other impurity elements. By using low-cost zinc powder as the reductant, TiOF₂ as the template, and ethanol as solution, Ti³⁺ is successfully self-doped into the bulk of 3D hollow nanoboxes, which are assembled by six ordered arranged TiO₂ nanosheet arrays with dominantly exposed {001} facets. In addition, due to strong visible adsorption by Ti³⁺ and oxygen vacancies, and charge recombination suppression, the RhB photodegradation activities were significantly enhanced under visible light irradiation.

2. Experimental

2.1. Topotactic synthesis process

TiOF₂ precursor was first prepared as a nanocubic template [20]. In a typical procedure, 5 mL HF was slowly added dropwise into 30 mL CH₃COOH under magnetic stirring. After stirring for 30 min, the mixed solution was added to a polyvinyl fluoride beaker containing 15 g tetrabutyl titanate (TBT). A white emulsion was obtained, which was then transferred to a dried 100-mL Teflon-lined autoclave and kept at 200 °C for 12 h. After being allowed to cool to 25 °C, the product was washed several times with ethanol and distilled water. The washed product was dried at 100 °C for 4 h to obtain a white TiOF₂ precursor.

Using TiOF₂ as the precursor, ethanol as a solvent, and zinc powder as a reducing agent, Ti³⁺ self-doped 3D hierarchical titanium dioxide hollow nanoboxes were prepared *via* a template-engaged *in-situ* topotactic transformation process. Typically, 1.0 g TiOF₂ and 0.05 g Zn were ground and added to 20 mL ethanol. Then the mixture was transferred to a Teflon-lined autoclave and kept in an oven at 200 °C for 24 h. After cooling, the powder was collected and washed with hydrochloric acid (38 wt%) under magnetic stirring to removal excess Zn. The washed powder was centrifuged and washed with distilled water until the pH ≈ 7. The centrifuged powder was dried overnight in a vacuum. The obtained product was marked as R0.05, where 0.05 indicates the Zn/TiOF₂ mass ratio. For comparison, different samples were also synthesized under identical conditions with various amounts of zinc. These samples are labeled R0, R0.2, R0.25, R0.3 and R0.4 [21–24].

2.2. Characterization

X-ray diffraction (XRD) measurements from the prepared powder were gathered using Cu K α radiation at a 2 θ scan rate of 0.02°/s with a D8-advance X-ray diffractometer (Bruker, Germany). The phase structure and crystal facets of the product were determined with a Tecnai G220 transmission electron microscope (TEM) (USA) operated at 200 kV acceleration voltage. Scanning electron microscope (SEM) images were gathered with a field emission scanning electron microscope (Hitachi, Japan). UV-vis diffuse reflectance spectroscopy (DRS)

measurements were gathered with a UV2600 (Shimadzu, Japan) UV-vis spectrophotometer, where BaSO₄ was used as the reference sample. The infrared spectra (IR) of the samples were measured using Fourier transform infrared spectroscopy (Nexus 470 FT-IR, Shimadzu, Japan). X-ray photo-electron spectroscopy (XPS) measurements were gathered with a Kratos XSAM800 XPS system with a monochromatic Mg *K*_α source and a charge neutralizer. All the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. Photoluminescence (PL) spectra were recorded with a fluorescence spectrophotometer (F-7000, Hitachi, Japan). Electron paramagnetic resonance (EPR) spectra were collected at room temperature with an EMX-8/2.7EPR spectrometer (Bruker, Germany).

2.3. Photocatalytic properties

A coumarin probe molecule PL technique was used to evaluate the photocatalytic activity of the samples. Coumarin readily reacted with •OH free radicals to produce highly fluorescent 7-hydroxycoumarin [25,26]. Typically, coumarin (0.5 mmol/L) was mixed with TiO₂ (1.0 g/L) under magnetic stirring, and the suspension was shaken for 24 h. A 150 W Xe lamp (Perkin-Elmer Co.), equipped with an ultraviolet cutoff filter, served as the visible light source. At given intervals, small samples were withdrawn and filtered through a membrane with a syringe. The photoluminescence spectra of the filtrate were obtained with a fluorescence spectrophotometer with 330 nm excitation wavelength.

Photocatalytic degradation of Rhodamine B (RhB) was performed out in a laboratory scale photoreactor at atmospheric pressure. About 50 mg of anatase Ti³⁺ self-doped 3D hollow nanoboxes (a concentration of 1 g/L) were added into an RhB solution (50 mL) with the initial concentration of 1.0×10^{-4} mol/L in a cylindrical Pyrex flask (50 mL). The Ti³⁺/RhB solution was first sonicated for 5 min and continuously stirred in darkness for 30 min. The photoreaction solution was illumi-

nated with the high pressure Xe lamp while stirring. UV-vis absorption spectra were recorded at successive intervals to monitor the photocatalytic reaction.

3. Results and discussion

3.1. Crystal planes and morphology

The crystal planes and morphology of the catalysts are major determinants of their photocatalytic properties. XRD spectra of the TiO₂ and Ti³⁺ self-doped samples are shown in Fig. 1. For all TiO₂ samples, a broad peak at $2\theta = 25.37^\circ$ was observed, corresponding to the {101} plane of anatase TiO₂ (JCPDS No. 21-1272). The peak at 24.05° is attributed to the diffraction peak of TiOF₂ and implies that all samples successfully completed the topotactic transformation process with the TiOF₂ template. No rutile patterns were formed in the as-prepared samples due to the presence of F⁻ ions as shape control agents [27,28]. As shown in Fig. 1, the peaks observed at $2\theta = 25.37^\circ$, 37.98° , 48.05° , 54.05° , and 55.08° correspond to diffraction from the {101}, {004}, {200}, {105}, and {211} crystal planes, respectively. These peaks are characteristic of anatase TiO₂. Compared with the undoped Ti³⁺ sample, diffraction peaks from the {004} and {105} crystal planes become sharper, while other crystal face diffraction peaks show little change. This can be ascribed an increased zinc concentration, leading to Ti³⁺ and O_v concentration increases. Each dopant may affect the {105} and {004} crystal faces differently. {105} crystal faces become more crystalline, whereas {004} crystal faces show lower crystallinity. In addition, the particle sizes (~260 nm) in various samples show little change. Meanwhile, the *d* space value remains constant, implying the reduced TiO₂ unit cell dimension is unlikely to change during the Ti³⁺ self-doping process.

The crystallite sizes for the {101} diffraction peak listed in Table 1 were determined from Scherrer equation: $D = K\lambda/(\beta\cos\theta)$. $K = 0.89$ is a shape factor, β is the full-width half-maximum of the diffraction peak, λ represents the wavelength of XRD (Cu *K*_α = 0.15418 nm), and θ is the XRD angle.

The morphology of the Ti³⁺ self-doped TiO₂ samples was examined using TEM, and the results are shown in Fig. 2. The insets in Fig. 2 show color photographs of the powdered samples. Fig. 2(a) shows a TEM image of pure TiO₂ (R0). The samples has a smooth surface, and hollow nanoboxes assembled from nanosheets are clearly visible. One can see in Fig. 2 (b)–(e) that the Ti³⁺ self-doped TiO₂ samples have well-defined box-shaped morphology, which is consistent with the cubic

Fig. 1. XRD patterns of Ti³⁺ self-doped TiO₂ samples with different Zn/TiOF₂ mass ratios, together with the expected diffraction peaks for standard TiOF₂ and anatase TiO₂ (S-TiOF₂, A-TiO₂).

Table 1
Structural analysis of various samples.

Sample	XRD ₍₁₀₁₎ relative intensity (%)	XRD ₍₁₀₁₎ peak position (°)	Crystal size ^a (nm)
R0	29	25.37	271
R0.05	34	25.35	269
R0.2	28	25.34	267
R0.25	37	25.30	255
R0.3	36	25.35	263
R0.4	31	25.31	265

^a The crystal sizes were calculated with Scherrer equation based on the {101} diffraction peak.

Fig. 2. TEM images and optical images (inset) of the as-prepared: R0 (a), R0.05 (b), R0.2 (c), R0.25 (d), R0.3 (e), and R0.4 (f). (f1) shows a high resolution TEM image of the R0.4 sample.

TiOF₂ template. With an increased amount of zinc powder, Ti³⁺ species were produced from Ti⁴⁺, but the sample morphology shows little change. The high resolution TEM image of sample R0.4 is shown in Fig. 2 (f1) with hollow nanoboxes erected on the Cu grid. The lattice spacing is about 0.235 nm, which agrees well with the {001} crystallite facet of anatase titanium dioxide. The top and bottom facets of the hollow boxes are also shown to be the {001} planes. In contrast with previously reported TiO₂ hollow structures, the as-prepared TiO₂ nanoboxes are hierarchical hollow nanoboxes consisting of six nanosheets with {001} facets. Ti³⁺ self-doping causes the number of Ti–O bonds to decrease, which increases the number of oxygen vacancies in the bulk of the nanoboxes rather than in the surface. It is exciting to find that the presence of zinc powder has a negligible effect on the morphology of 3D TiO₂ hollow nanoboxes. The surface adsorbed ZnO clusters disappear after acid treat-

ment, which are usually thought to be responsible for the stability of the reduced TiO₂. The color of the as-prepared samples turned from pure white to dark blue, and the blue coloration became much darker with an increased amount of zinc (inset of Fig. 2). The blue coloration of the Ti³⁺ self-doped TiO₂ samples is attributed to an increased concentration of Ti³⁺ or O_v obtained from reduction of Ti⁴⁺ by the zinc powder, which is consistent with results reported in the literature [29].

Fig. 3 shows SEM images of the Ti³⁺-doped TiO₂ samples. The images in Fig. 3(a)–(e) show uniformly shaped hollow boxes whose structures originate from the TiOF₂ nanocube template. The boxes are enclosed by six well-arranged TiO₂ nanosheets with many sheets stacked.

EDS images of the R0.25 catalysts are shown in Fig. 4. The four panels on the left are elemental face-scans of the inset image. The presence of Ti and O is obvious, as indicated by red

Fig. 3. SEM images of Ti³⁺ self-doped TiO₂ samples. (a) R0, (b) R0.05, (c) R0.2, (d) R0.25, (e) R0.3, (f) R0.4.

Fig. 4. The face-scan and spot-scan SEM images and EDS analysis of the R0.25 sample.

Table 2

The EDS spot-scan data of the R0.25 sample.

Elements	Line	Intensity (c/s)	Atomic (%)	Conc (wt%)
O	K_{α}	61.62	65.87	40.593
Ti	K_{α}	317.43	34.13	59.407

dots and green dots, respectively. The right picture shows spot-scan elemental content in the red-marked area, which was found to contain Ti and O. As shown in Table 2, the atomic concentration of Ti and O in the R0.25 sample can reach 34.13% and 65.87%, respectively. This is consistent with atomic ratio of TiO_2 .

A probable formation mechanism of Ti^{3+} self-doped 3D TiO_2 hollow nanoboxes has been proposed *via* a topological transformation process involving template participation, as shown in Fig. 5. Ethanol is used as a solvent to provide mild reaction conditions. TiOF_2 cube templates will transform into TiO_2 during a solvothermal reaction by *in situ* transformation of TiOF_2 to anatase TiO_2 nanocrystals (Eqs. (1) and (2)). It has been reported that fluoride ions facilitate the formation of high-energy anatase TiO_2 nanosheets because the adsorption of F^- on the surface of TiO_2 nanocrystals can sharply reduce the surface energy of the {001} facets. Therefore, it is understandable that precursor TiOF_2 can transform into anatase 3D TiO_2 hollow

Fig. 5. The probable formation process of Ti^{3+} self-doped 3D TiO_2 hollow nanoboxes.

nanoboxes *in situ* assembled from TiO_2 nanosheets with exposed high-energy {001} facets. Zn powder acts as reductant. It has been found that Zn can affect the morphology of TiO_2 , and the surface-adsorbed ZnO clusters are thought to be responsible for the stability of the Ti^{3+} -doped TiO_2 (Eq. (3)). In the reducing atmosphere, Ti^{3+} can be easily obtained *via* reduction of Ti^{4+} along with generation of O_v sites, which will produce donor states just below the conduction band [20,21].

3.2. UV-vis, FT-IR, EPR and XPS results

As showed in Fig. 6(a), UV-vis diffuse reflectance spectra were used to measure the optical properties of the obtained Ti^{3+} self-doped TiO_2 hollow nanoboxes. The undoped TiO_2 sample (R0) shows no absorption above its fundamental absorption edge, while the reduced TiO_2 samples display broad visible light absorbance after Ti^{3+} self-doping, and the absorption intensities of all Ti^{3+} self-doped TiO_2 samples is gradually enhanced as zinc concentration increases. It is widely accepted that the Ti^{3+} -doped modification and the presence of oxygen vacancies can induce the formation of color centers, which results in enhanced visible light absorption. To further investigate the band gap in each sample, the energy gap (eV) threshold was obtained using the transversal method, and the graph of the transformed Kubelka-Munk function against the photon energy for samples R0 and R0.25 are displayed in Fig. 6(b). According to the transformed Kubelka-Munk function plot, the energy gaps of $E_{g(\text{R0})}$ and $E_{g(\text{R0.25})}$ are 3.02 and 2.94 eV, respectively. The reduced bandgap arises because Ti^{3+} can form a local energy state between the valence and conduction bands as Ti^{3+} concentration increases, which reduce the forbidden band width and the electron transition energy. In addition, the color of the as-prepared samples shifts gradually from white to dark blue, and the blue coloration indicates strong visible light absorption in the Ti^{3+} self-doped samples. Meanwhile, we find that the Ti^{3+} self-doped samples also exhibit very strong UV absorption, which indicates Ti^{3+} self-doping not only enhances the visible light response of the catalysts, but also improves their UV light absorption. Thus, it can be predicted that more photo-generated electrons and holes can be excited and can

Fig. 6. (a) UV-vis diffuse reflectance spectra of Ti^{3+} self-doped TiO_2 samples. (b) Plot of transformed Kubelka-Munk function versus photon energy for the R0 and R0.25 samples.

participate in photocatalytic reactions, which is attributed to the increased probabilities of activation by UV and visible light.

FT-IR spectra of the Ti^{3+} self-doped samples were gathered to further verify the presence of Ti^{3+} and oxygen vacancies, as shown in Fig. 7(a). The stretching and bending vibrations due to absorption by H_2O and the Ti-OH group on the sample surface are found near 3447 and 1629 cm^{-1} , respectively. The stretching vibration of Ti-O-Ti is observed at 1380 cm^{-1} , and the Ti-O bond stretching vibration is observed from 547 to 524 cm^{-1} . This peak is shifted 23 cm^{-1} to longer wavelengths, and the shift can be attributed to the formation of Ti^{3+} and oxygen vacancies. This can be explained based on formation of Ti^{3+} due to reduction of Ti^{4+} . The increased number of oxygen vacancies (O_v) in the lattice structure changes the number of Ti atom surrounding an O atom, and the electron cloud density around a Ti atom decreased. This causes the stretching vibration absorption peak of a Ti-O bond to shift. This demonstrates that Ti^{3+} self-doping introduces more Ti^{3+} ions and O_v into the bulk of the 3D hollow nanoboxes rather than at the surface.

EPR spectra were also recorded to further verify the gener-

ation of Ti^{3+} in the R0 and R0.25 samples. As shown in Fig. 7(b), paramagnetic Ti^{3+} and O_v have g -values of 1.98 and 2.00 in the R0.25 sample, respectively. These values are consistent with reports that Ti^{3+} and O_v peaks are found at $g = 1.94\sim 1.99$ and 2.004 , respectively [24–30]. As we all know, the surface Ti^{3+} is not stable under illumination in water or air as it is easily oxidized, which shows an EPR signal at $g = 2.02$ corresponding to O_2^- . Therefore, the absence of such a peak in Fig. 7(b) indicates that Ti^{3+} is present in the bulk rather than on the surface, which is attributed to its high stability in water or air. During hydrothermal treatment, with increasing Zn concentration, sample R0.25 shows higher Ti^{3+} doping concentration than sample R0.

XPS measurements were gathered to further investigate the chemical environment of Ti^{3+} -doped TiO_2 . As shown in Fig. 8, the high-resolution XPS spectrum of $\text{Ti } 2p$ for R0.25 displays two peaks at binding energies of 459.01 eV ($\text{Ti } 2p_{3/2}$) and 464.85 eV ($\text{Ti } 2p_{1/2}$). The $\text{Ti } 2p$ binding energy peaks can be divided into four peaks at 458.63 eV ($\text{Ti}^{3+} 2p_{3/2}$), 463.88 eV ($\text{Ti}^{3+} 2p_{1/2}$), 459.19 eV ($\text{Ti}^{4+} 2p_{3/2}$), and 464.89 eV ($\text{Ti}^{4+} 2p_{1/2}$). It should be emphasized that there are no zinc binding energy

Fig. 7. FT-IR (a) and EPR (b) spectra of different samples.

Fig. 8. The XPS spectra of the R0.25 sample.

peaks in high resolution XPS spectrum. These peaks may be absent from the XPS spectra if the surface-adsorbed zinc clusters can be completely removed from the surface of Ti^{3+} -doping TiO_2 after acid treatment. The O 1s peaks at 529.87 and 530.16 eV are ascribed to the Ti–O bond and O_v adjacent to Ti^{3+} , respectively. From Table 3, it can be found that Ti^{3+} -doping in sample R0.25 increases the electron binding energy of Ti and O by about 0.30 and 0.29 eV respectively, compared with sample R0. It is well accepted that the presence of Ti^{3+} and O_v can suppress recombination of photo-generated electron-hole pairs, improve the formation rate of photo-induced hydroxyl radicals, and enhance the visible light response.

3.3. Visible-light photocatalytic performance

Visible-light photocatalytic activities of the as-prepared samples were investigated by RhB degradation to explore the effect of Ti^{3+} self-doping. It can be seen from Fig. 9(a) that self-degradation of RhB can be negligible, and the visible-light degradation activities of the Ti^{3+} self-doped TiO_2 samples indicates much higher photocatalytic efficiencies than undoped TiO_2 (R0) under visible light irradiation ($\lambda \geq 420$ nm). This effect depends on the concentration of RhB versus visible light irradiation time. The R0.25 sample shows the highest photocatalytic activity with an RhB degradation rate of 96% after 2 h of visible light irradiation, resulting from its higher concentration of Ti^{3+} and O_v . However, pure TiO_2 (R0) shows a low decomposition rate of RhB under the same reaction conditions. It can be demonstrated that the photodegradation rate of Ti^{3+} self-doped TiO_2 is proportional to the doped Ti^{3+} concentration in the bulk of hollow nanoboxes, which is dependent on visible absorption (Fig. 9(a)). The experimental result indicates that Ti^{3+} self-doping is an effective method to enhance the visible photocatalytic activity of TiO_2 hollow nanoboxes for degradation of organic pollutants. It is generally accepted that the slopes of the RhB intensity curves versus illumination time (rate constant) represent the photocatalytic activity of the

samples. By comparing the rate constants of the photocatalysts (Fig. 9(b)), we can see that the rate constants of the samples first increase and then decrease as the zinc powder/ TiO_2 mass ratio increases. As observed from the histogram of rate constants in Fig. 9(b), we find that the R0.25 sample reveals the highest visible-light photocatalytic activity (rate constant of 0.02394). This value is 4.0 times higher than the rate constant for undoped TiO_2 (R0) (rate constant of 0.00596).

To further evaluate the visible-light photocatalytic activity of the samples, coumarin is used as a probe molecule to explore the production rate of hydroxyl free radicals ($\cdot\text{OH}$ is the most important active species in the photocatalytic reaction) from

Fig. 9. (a) Dependence of the RhB concentration on visible light irradiation time. (b) Comparison of the rate constants.

Table 3

Electron binding energy of R0 and R0.25 samples.

Sample	Ti 2p (eV)	O 1s (eV)
R0	458.71	529.87
R0.25	459.01 (Ti^{3+} 458.63 eV, 463.88 eV; Ti^{4+} 459.19 eV, 464.89 eV)	530.16

Fig. 10. (a) PL spectral changes observed during illumination of the R0.25 sample. (b) $\cdot\text{OH}$ production rate constants for different samples. (c) Fluorescence detection of superoxide free radical (O_2^-) in the R0.25 sample.

the Ti^{3+} self-doped TiO_2 samples under the visible light irradiation [30,31]. Fig. 10(a) records typical photoluminescence spectral changes in the R0.25 sample over different illumination times. One can see that the photoluminescence intensity of the photo-induced fluorescent 7-hydroxycoumarin at 450 nm increases as the irradiation time increases when the samples are excited at 330 nm. The $\cdot\text{OH}$ production rate constants (the slope of the PL intensity vs illumination time curve) for the Ti^{3+} self-doped TiO_2 samples are shown in Fig. 10(b), which represents the photocatalytic activity of the samples. It can be seen that the rate constant of the catalyst first increases and then decreases as the Zn/TiOF_2 mass ratio increases. The R0.25 sample exhibits the highest photodegradation activity and is much better than the undoped TiO_2 catalyst (R0), which is consistent with RhB photodegradation measurements. Fig. 10(c) shows typical active species super oxygen free radical (O_2^-) photoluminescence spectra from sample R0.25, which indicates that the emission wavelength is 550 nm. The fluorescence intensity and the O_2^- constantly increased with increasing illumination time, which implies that sample R0.25 under visible light irradiation produces O_2^- .

In order to further investigate the stability of Ti^{3+} self-doped TiO_2 catalysts, the R0.25 catalyst, which displays the highest rate constant, was recycled five times after bleaching the RhB under visible irradiation. One can see that the photodegradation rate of RhB reduces, but remains at 81% after 5 cycles, as

shown in Fig. 11. Thus, the photocatalytic stability is acceptable under visible light irradiation, indicating there are very few Ti^{3+} ions on the surface of the TiO_2 sample. These ions are unstable and can be oxidized to Ti^{4+} . In comparison, the high stability of our catalyst demonstrated the vast majority of Ti^{3+} and O_v were introduced into the lattice of the 3D hollow nanoboxes rather than at the surface.

3.4. Reasons for enhancement of the visible light response

According to a previous report, doped TiO_2 powders can form two phases [32]. Generally, two phases for the same semiconductor composite have great benefits in suppressing recombination of photo-induced holes and electrons pairs, which enhances the photocatalytic properties [33–35]. We use PL measurements to evaluate whether recombination of photo-generated electron-hole pairs on the surface of Ti^{3+} self-doped TiO_2 was effectively inhibited after Ti^{3+} doping. Herein, PL analyses for the un-doped (R0) and Ti^{3+} self-doped TiO_2 samples (R0.05, R0.2, R0.25, and R0.3) were conducted. As shown in Fig. 12, we find the shape of the emission spectra are very similar for all samples, and all spectra consist of four primary peaks. The highest intensity peak at ~ 387 nm is attributed to the radiative transition, while the other three weaker peaks, ranging from 440 to 520 nm, are ascribed to surface

Fig. 11. Cycling degradation of RhB over the R0.25 sample under visible light irradiation.

Fig. 12. PL spectra for different samples.

Fig. 13. Possible photocatalytic mechanism of Ti^{3+} self-doped TiO_2 .

oxygen vacancies [36]. The photoluminescence intensity for sample R0.25 is lower than that for the undoped Ti^{3+} (R0) sample. This result in turn confirms the strong interaction present in the R0.25 sample due to suppression of the radiative recombination process. Therefore, it is reasonable to predict that the Ti^{3+} self-doped R0.25 sample would exhibit superior photodegradation activity than undoped TiO_2 (R0).

3.5. Photocatalytic mechanism

Considering the superior photocatalytic activity of Ti^{3+} self-doped TiO_2 hollow nanoboxes, we propose the possible mechanism shown in Fig. 13. Generally, the TiO_2 -based catalytic reaction generated electron-hole pairs (e^- - h^+) during illumination. In contrast, for the Ti^{3+} self-doped TiO_2 catalyst, the bandgap reduction in the Ti^{3+} self-doped TiO_2 catalyst greatly reduces the excitation power and enhances the visible light response. Meanwhile, the Ti^{3+} -doping states can trap photo-induced electrons and transfer them to oxygen adsorbed on the surface of the catalyst. Thus, the existence of a certain number of Ti^{3+} states can decrease the recombination rate of photo-generated electron-hole pairs and promote photocatalytic activity. If the concentration of Ti^{3+} is too high (e.g., as in R0.3 and R0.4), the recombination rate of photo-induced charges will increase, resulting in a decreased distance between the Ti^{3+} trapping states and Ti^{3+} dopants [37,38].

4. Conclusions

In summary, we have proposed a simple topotactic method for preparing Ti^{3+} self-doped 3D TiO_2 hollow nanoboxes with dominant high energy {001} facets using a one-pot hydrothermal reduction method in the presence of zinc powder and TiOF_2 . The presence of Ti^{3+} species has little effect on the morphology, which keeps the hollow nanoboxes originating from the TiOF_2 template. The Ti^{3+} self-doped TiO_2 sample with Zn/ TiOF_2 mass ratio of 0.25 shows the highest rate of RhB photodegradation (96%) after 2 h of visible light irradiation. This value is 4.0 times than that of pure TiO_2 hollow nanoboxes due to the introduction of Ti^{3+} and O_v , which enhanced visible

light photocatalytic activity. The present study provides a simple approach for designing high efficiency visible-light-responsive Ti^{3+} self-doped TiO_2 photocatalysts with 3D hierarchical hollow structures.

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Graphical Abstract

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One-pot topotactic synthesis of Ti^{3+} self-doped 3D TiO_2 hollow nanoboxes with enhanced visible light responseChengjiang Zhang, Lijun Tian, Lianqin Chen*, Xiaofang Li, Kangle Lv, Kejian Deng
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Ti^{3+} self-doped anatase TiO_2 catalysts, with 3D hollow nanobox structure, were prepared via a template-engaged topological transformation process by a one-pot hydrothermal method. The introduction of Ti^{3+} and oxygen vacancies greatly enhanced the visible photocatalytic activity.

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拓扑相变制备具有拓宽可见光响应范围的 Ti^{3+} 自掺杂3D空盒状 TiO_2 张成江^a, 田丽君^a, 陈连清^{a,*}, 黎小芳^b, 吕康乐^a, 邓克俭^a^a中南民族大学催化材料科学国家民委-教育部重点实验室, 湖北武汉 430074^b武汉科技大学化学化工学院, 湖北武汉 430081

摘要: TiO_2 广泛用作半导体光催化材料, 但由于自身对光利用率低(只吸收紫外光)、禁带宽度较大、光生载流子复合率极高, 限制了它在相关领域的应用。为此, 设计了 Ti^{3+} 离子自掺杂来克服 TiO_2 半导体材料的上述缺点, 进而提高其光催化活性。在不引入其他元素的情况下, 以 TiOF_2 为原料, Zn 粉为还原剂, 在水热条件下采用拓扑相变法原位制备了具有可见光响应的 Ti^{3+} 自掺杂空盒状 TiO_2 (记为 $\text{Ti}^{3+}/\text{TiO}_2$) 催化剂材料。掺杂金属离子可以改变半导体 TiO_2 的结晶度和产生晶格缺陷, 形成电子或空穴的捕获中心, 影响电子-空穴对的复合; 同时, 掺杂金属离子产生的晶格缺陷有利于 Ti^{3+} 和氧空位的形成, 有利于提高 TiO_2 的量子效率。 Ti^{3+} 掺杂是一种既清洁又未引入其他金属离子的掺杂改性方法, 它能有效保持催化剂的结构和形貌不受其他金属离子的影响。总之, 金属离子掺杂有效拓展了 TiO_2 的光吸收范围, 并极大地提高了 TiO_2 的光催化活性。

本文研究了不同量的还原剂对催化剂空盒状 TiO_2 结构形貌影响, 以及在可见光下光催化降解罗丹明B反应性能, 发现 $\text{Ti}^{3+}/\text{TiO}_2$ 催化剂均拥有非常好的光催化活性, 其中R0.25催化剂在可见光下120 min, RhB降解率达到96%, 是 TiO_2 的4倍多。

且可循环使用5次的光催化循环降解实验后,表现出较高的稳定性. 催化剂经过 Ti^{3+} 自掺杂后,对催化剂自身的空盒状结构形貌并无很大的影响,随着还原剂Zn粉的量增加, Ti^{4+} 还原形成 Ti^{3+} 数量增加,导致形成更多的氧空位. 皆为锐钛矿型 TiO_2 ,与未掺杂 Ti^{3+} 的 TiO_2 比较发现,自掺杂 Ti^{3+} 的 TiO_2 的(105)XRD衍射峰越来越尖锐,(004)衍射峰越来越宽. 随着还原剂Zn粉质量的逐渐增加,催化剂的光响应范围拓宽到可见光区,且逐渐增强. 这说明 Ti^{3+} 的掺杂不仅提高了 TiO_2 在可见光的响应能力,也提高了 TiO_2 在紫外光范围的响应能力. 另外,掺杂后的 TiO_2 禁带宽度的减小,使其价带上的电子更容易被可见光激发,产生更多的电子-空穴对参与光催化反应,从而提高 TiO_2 的光催化效率.

关键词: Ti^{3+} 自掺杂; 拓扑相变; 3维空盒子; 可见光响应; 光催化活性

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