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Article

Preparation of Ti^{3+} self-doped TiO_2 nanoparticles and their visible light photocatalytic activity

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ABSTRACT

Ti^{3+} self-doped TiO_2 nanoparticles were synthesized by hydrothermal treatment of a gel precursor obtained using TiH_2 as the Ti source and H_2O_2 as oxidant. The effects of different states of gel and hydrothermal treatment time on the properties of the samples were studied. The structure, crystallinity, morphology, and optical properties of the nanoparticles were characterized by X-ray diffraction, transmission electron microscopy, high-resolution transmission electron microscopy, and UV-visible diffuse reflectance spectroscopy. The chemical states of Ti and O were confirmed by X-ray photoelectron spectroscopy and electron spin resonance spectroscopy. Methylene blue (MB) solutions were used as simulated wastewater to evaluate the visible-light photocatalytic activity of the samples. The samples exhibited strong absorption in the visible light region compared with pure TiO_2 and an excellent performance in the photocatalytic degradation of MB. When yellow gel was used as the precursor, the sample obtained after hydrothermal treatment at 160 °C for 24 h exhibited the best visible light photocatalytic activity with a reaction rate constant of 0.0439 min^{-1} , 18.3 times that of pure TiO_2 . The samples also showed excellent cyclic stability of the photocatalytic activity.

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1. Introduction

TiO_2 is one of the most promising semiconductor photoelectric conversion materials due to its excellent chemical stability and nontoxicity [1]. However, the band gap of anatase phase TiO_2 is 3.2 eV, which limits it to the absorption of ultraviolet light, which makes up less than 5% of sunlight. Hence, it is crucial to enhance the light harvesting of TiO_2 in the visible region, which accounts for more than 43% of total solar energy. Although many methods, such as ion doping, noble metal modifi-

cation, surface plasmon enhanced absorption, organic dye sensitization, and semiconductor compositing, have been used to solve this problem, they do not fundamentally solve the low photoelectric conversion efficiency of TiO_2 [2–7]. The electron transfer rate of pure TiO_2 is low ($0.1\text{--}4 \text{ cm}^2\cdot\text{V}\cdot\text{s}^{-1}$), and lattice defects and doping impurity defects tend to reduce the thermal stability of TiO_2 and increase the number of carrier recombination centers, which may decrease the overall photoelectric conversion efficiency [8,9]. Therefore, the design of TiO_2 having both visible light excitation and rapid photoinduced electron

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transfer has always been of great interest.

Previous studies have shown that Ti^{3+} self-doped TiO_2 can be excited by visible light [10]. Meanwhile, Ti^{3+} ions give the TiO_2 good electronic conductivity, which is very important for improving its photoelectric conversion efficiency [11,12]. However, based on the electrode potential, the reduction of Ti^{4+} to Ti^{3+} is difficult under normal conditions, and the resulting Ti^{3+} is very easily re-oxidized to Ti^{4+} [13,14]. At present, most methods of preparing Ti^{3+} self-doped TiO_2 are based on "reduction", by heating the TiO_2 in vacuum or a strong reducing atmosphere such as H_2 , CO, or by bombarding the TiO_2 with high-energy particles (electrons, argon ions) [15–17]. These methods have some limitations to their practical application, such as multiple reaction steps, harsh conditions, long reaction time and expensive equipment, etc. Moreover, because reduction reactions usually occur on the surface of TiO_2 particles, the obtained Ti^{3+} can easily be oxidized by O_2 in air or dissolved oxygen in water, reducing the stability of Ti^{3+} self-doped TiO_2 [14]. Although the preparation of Ti^{3+} self-doped TiO_2 by reducing Ti^{4+} in mild liquid phase has been reported, the generation of by-products during the reaction process meant that subsequent treatments were needed to obtain pure Ti^{3+} self-doped TiO_2 [18,19]. Thus, it is still a great challenge to develop a simple and economic strategy to synthesize stable Ti^{3+} self-doped TiO_2 nanoparticles.

According to the corresponding electrode potential (Ti^{3+} , Ti^{2+} , $A = -0.37 \text{ V}$), Ti^{2+} is easily oxidized to Ti^{3+} . Therefore, we have adopted an oxidation-based method to prepare Ti^{3+} self-doped TiO_2 nanomaterials in aqueous solution using the water- and air-stable industrial raw material TiH_2 as the Ti source. TiH_2 has a unique advantage as a raw material, namely, Ti^{3+} self-doped TiO_2 is easily obtained by controlling the oxidation of Ti^{2+} to Ti^{3+} , completely avoiding the need for the harsh conditions and long reaction time required when using H_2 or CO to reduce Ti^{4+} to Ti^{3+} [20,21].

In our previous work, we used H_2O_2 to oxidize TiH_2 and obtained a yellow-green precursor gel, after which different treatment methods were used to produce Ti^{3+} self-doped TiO_2 [22]. The amount of H_2O_2 , the oxidation time, and other factors were not considered in the gel preparation process. The reaction of Ti^{4+} and H_2O_2 creates complex ions with different compositions, which would affect the types and amounts of oxygenated compounds generated on the TiH_2 surface during the gel preparation process, thereby affecting the final product performance. In this paper, the amount of H_2O_2 and the oxidation time were controlled to obtain two different states of precursor gel, and the gels were hydrothermally treated at 160°C for different times. The relationship between the structures and photocatalytic performance of the different products obtained from the different precursor gels were studied in detail. The structure, morphology, and other properties of the samples were studied using X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR) spectroscopy, and UV-visible diffuse reflectance spectroscopy (UV-Vis DRS). Methylene blue (MB) solutions were used as simulated wastewater to evaluate the visible-light

photocatalytic activity of the samples.

2. Experimental

2.1. Photocatalyst preparation

The precursor gel preparation process was similar to that described in our preliminary study [20], except that yellow and green precursor gels were obtained by controlling the amount of H_2O_2 and the oxidation time. The precursor gels were transferred to dry Teflon-lined autoclaves, and then heated to 160°C for different times. After natural cooling to room temperature, the gray-blue or light-blue mixture was collected and washed with distilled water and ethanol three times, and then dried in an oven at 60°C for 3 h. The products obtained from the yellow gel are labeled as Y-t, while the products obtained from green gel are labeled as G-t, where t indicates the hydrothermal treatment time (hours). For comparison, pure TiO_2 (denoted p- TiO_2) was obtained by hydrothermal treatment at 160°C for 24 h using TiCl_4 as the Ti source.

2.2. Characterization

The phases of the final products were identified using XRD (Rigaku D/max-2500VPC) with graphite monochromated $\text{Cu } K_\alpha$ ($\lambda = 0.15418 \text{ nm}$) radiation at a scanning rate of $0.02^\circ/\text{s}$. A Hitachi H-800 model TEM and JEOL JEM-2100 model HRTEM were used to determine the size and shape of the particles. TEM sample specimens were prepared by briefly ultrasonically dispersing the sample powders in ethanol, followed by placing a drop of suspension onto a carbon-coated copper grid. The grids were dried before imaging. XPS measurements were carried out on an X-ray photoelectron spectrometer (ESCA 3000) using $\text{Al } K_\alpha$ (1486.6 eV) X-rays as the excitation source. $\text{C } 1s$ (284.6 eV) was chosen as the reference. ESR measurements were carried out using a FA-200 spectrometer/X-bond. UV-vis DRS were recorded on a Shimadzu UV-2550 UV-vis spectrophotometer in the range 200–800 nm at room temperature, with a BaSO_4 standard used as the reference.

2.3. Photocatalytic activity measurements

The photocatalytic activities of the as-prepared samples were evaluated using the photodecomposition of MB solution under visible light irradiation at room temperature. The visible light was provided by a 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co., Ltd.) equipped with an ultraviolet cutoff filter (UVCUT 400, Beijing Trusttech Co., Ltd.). The vertical distance between the surface of the sample suspension and the light source was set at 30 cm. In a typical photocatalytic experiment, 0.06 g of sample was dispersed into 100 mL MB solution ($2 \times 10^{-5} \text{ mol/L}$) under constant stirring. The suspension was stirred for 30 min in the dark prior to irradiation. Aliquots of about 3 mL were removed from the suspension at 10 min intervals during visible light illumination and centrifuged to remove the remaining particles. The absorbance of the centrifuged solutions was measured at 500–800 nm as a function of

irradiation time by UV-vis spectroscopy (UV-7200, Unico, Shanghai).

3. Results and discussion

3.1. Phase analysis

XRD was used to investigate the structural changes and phase purity of the samples obtained from the different precursor gels after different hydrothermal treatment times at 160 °C, as shown in Fig. 1. When the hydrothermal treatment time was 20 h, the content of TiH_2 in the products obtained from the yellow precursor gel was lower than that of the products obtained from the green precursor gel. Except for two weak diffraction peaks of TiH_2 at $2\theta = 34.9^\circ$, 40.6° [JCPDS 65-0934], all the observed diffraction peaks corresponded to those of anatase TiO_2 (JCPDS 21-1272). However, the content of TiH_2 was very high in the products obtained using the green gel as the precursor. The yellow gel precursor transformed to pure anatase TiO_2 after 24 h hydrothermal treatment, compared with 27 h for the yellow green gel [22], while the green gel still contained a small amount of TiH_2 after 27 h, and only became pure anatase phase TiO_2 after the treatment time was extended to 32 h.

In the presence of H_2O_2 , Ti^{4+} is known to exhibit different colors at different pH in a system; orange in acidic conditions, yellow at pH ~ 8 , and colorless in strong alkaline conditions. In the present gel preparation process the pH value remained neutral, so the different states of gel obtained were caused by the presence of different proportions of Ti-oxygen compounds produced by oxidation of H_2O_2 on TiH_2 . The lower content of TiH_2 in the yellow gel indicated that the TiH_2 was oxidized to a high degree in the yellow gel, making it easier to completely transform to TiO_2 during the hydrothermal treatment. In the green gel, the degree of oxidation was low and the content of TiH_2 was high, so it took a long time for it to transform into TiO_2 during the hydrothermal treatment. In addition, no matter

Fig. 1. XRD patterns of the samples obtained from different gels after hydrothermal treatment at 160 °C.

what kind of gel was used as the precursor, the TiO_2 diffraction peaks became increasingly sharp with increasing hydrothermal treatment time, indicating a corresponding better crystallinity and larger crystallite size of the obtained TiO_2 . Therefore, when using TiH_2 as the Ti source and H_2O_2 as oxidant to prepare Ti^{3+} self-doped TiO_2 , controlling the oxidation time and degree of oxidation to obtain the yellow gel precursor shortens the time required for the subsequent hydrothermal treatment.

3.2. Morphology observations

Fig. 2 shows TEM and HRTEM images of the samples obtained after hydrothermal treatment at 160 °C for different times. Sample Y-20 was composed of small particles (Fig. 2(a)). Because the content of TiH_2 in this sample was very small, the lattice structure of TiH_2 could not be observed in the HRTEM image. When the hydrothermal treatment time was prolonged

Fig. 2. TEM and HRTEM images of samples obtained from different gels after hydrothermal treatment at 160 °C. (a) Y-20; (b) Y-24; (c,d) G-20; (e,f) G-32.

to 24 h, the morphology of the sample become more regular, and the dispersity was improved (Fig. 2(b)). The XRD results indicated that this sample was pure anatase phase TiO_2 (Fig. 1). Under the same conditions, the sample obtained using the green gel as the precursor was irregular in shape after hydrothermal treatment for 20 h, with a wide particle size distribution (Fig. 2(c)). HRTEM showed that TiH_2 was still present in this sample; the spacing $d = 0.44$ nm in Fig. 2(d) is TiH_2 [23]. The TEM and HRTEM results further indicated the products formed from the green gel precursor after shorter hydrothermal treatment times were composites of TiH_2 and TiO_2 . The morphology of the samples became more regular with increasing hydrothermal treatment time. When the hydrothermal treatment time was 32 h, the sample obtained from the green gel precursor had a well-defined morphology and good dispersity (Fig. 2(e)). The HRTEM results show that this sample was pure anatase phase TiO_2 (Fig. 2(f)), in agreement with the XRD results. The particle sizes of the samples obtained from the yellow gel were the smallest, while those of the samples obtained from the green gel were the largest. In heterogeneous photocatalytic processes, small particles have good dispersity and strong adsorption ability, and can provide a greater number of active sites for the adsorption of pollutant molecules, which is conducive to photocatalytic reactions [24].

3.3. XPS and ESR analyses

XPS and EPR were used to determine the composition and the chemical state of Ti in the samples. Fig. 3(a) and (b) present high resolution Ti 2p and O 1s XPS results for samples Y-20, Y-24, and G-32. Fig. 3(c) and (d) present the Ti 2p and O 1s fitting results of samples G-32 and Y-24, respectively. Pure TiO_2 had typical Ti 2p binding energies of ~ 464.5 and ~ 459.0 eV [25], while those of Y-20 and Y-24 were shifted to lower energy owing to the presence of Ti^{3+} in the samples [17]. This shift to lower energy was decreased with increasing hydrothermal treatment time, indicating that the concentration of Ti^{3+} in the samples decreased with increasing hydrothermal treatment time. The Ti 2p peaks were well de-convoluted into four peaks as $\text{Ti}^{3+} 2p_{3/2}$ at 457.7 eV, $\text{Ti}^{4+} 2p_{3/2}$ at 458.7 eV, $\text{Ti}^{3+} 2p_{1/2}$ at 463.0 eV, and $\text{Ti}^{4+} 2p_{1/2}$ at 464.5 eV [25,26] for the sample ob-

Fig. 4. ESR spectra for different samples.

tained after treatment of the green gel precursor at 160 °C for 32 h (Fig. 3(c)), but the strength of the Ti^{3+} binding energy peak was weak, indicating that the content of Ti^{3+} was low.

The binding energy of O in the Ti–O band is located at 529.5–530.5 eV [27]. Fig. 3(d) shows the high resolution O 1s XPS spectra of the samples. This binding energy appeared at 530 eV for all three samples, indicating that O existed mainly in the form of Ti–O, but the peaks were asymmetrical. Three peaks were obtained after fitting the peak of sample Y-24 (Fig. 3(d)). The binding energy at 530.1 eV corresponds to the Ti–O band, while the peak at 531.3 eV corresponds to the characteristic peak of surface oxygen defects (Ov) [28]. The weak peak at 532.3 eV corresponds to the characteristic peak of the –OH band [29,30], indicating that –OH existed on the surface of the particles.

ESR was used to study the uncoupled electrons in the samples and their interactions with the surrounding atoms in the material. Fig. 4 shows the ESR results of samples Y-20, Y-24, G-27, G-32, and pure TiO_2 . Compared with pure TiO_2 , a signal peak at about $g = 1.94$ appeared for all of the samples after hydrothermal treatment, corresponding to the Ti^{3+} signal peak. The intensity of this signal peak decreased with increasing hy-

Fig. 3. High-resolution XPS spectra of Ti 2p (a) and O 1s (b) for different samples. Fitting results of Ti 2p (c) for sample G-32 and O 1s (d) for sample Y-24.

drothermal treatment time, indicating that the Ti^{3+} concentration in the sample decreased [31], which is consistent with the XPS results. An electron trapped on an Ov would produce a signal at $g = 2.003$; this signal peak indicates the presence of surface Ti^{3+} [32], and shows that Ti^{3+} not only existed in the lattice, but also in the surface of the samples. The decreasing content of Ti^{3+} and Ov in the samples observed with increasing hydrothermal treatment time is consistent with the XPS results.

The presence of Ti^{3+} , Ov, and $-\text{OH}$ groups on the surface of TiO_2 has important effects on the photoelectric conversion properties of the material. Surface $-\text{OH}$ groups are able to capture holes to form oxidizing hydroxyl radicals ($\bullet\text{OH}$), which play an important role in the photocatalytic degradation of organic pollutant molecules [33,34].

3.4. Optical absorption properties

Fig. 5 shows the UV-vis DRS spectra of the Ti^{3+} self-doped TiO_2 nanoparticles obtained under different conditions and pure TiO_2 . Unlike p- TiO_2 , the spectra of the Ti^{3+} self-doped TiO_2 samples exhibited a broad absorption band between 400–800 nm, covering the entire visible range. Samples Y-20 and G-27 had strong absorptions in the visible light region, but weak in the UV region. On the one hand, this was caused by the presence of incompletely reacted TiH_2 in the samples, while on the other hand, because the hydrothermal treatment time was short, Y-20 and G-27 had poor crystallinity and more defects. The UV absorption of the samples was enhanced by prolonging the hydrothermal treatment time for both the yellow and green gel precursors. This is because the crystallinity of the samples continuously improved with treatment time, while the amount of defects decreased. Additionally, samples Y-24 and G-32 had strong absorption both in the visible and UV regions, indicating that these samples had good crystallinity, fewer defects, and more Ti^{3+} . Sample Y-24 had a stronger absorption in the visible light range than sample G-32, indicating a higher concentration of Ti^{3+} in sample Y-24 than G-32, consistent with the XPS and ESR results.

Fig. 5. UV-Vis-DRS spectra for different samples.

According to the above results, we believe that the Ti^{2+} on the surface of the TiH_2 particles was gradually oxidized by H_2O_2 , and a number of oxygenated Ti compounds and their hydrates were formed at the particle surface. When the hydrothermal treatment was carried out on the precursor gel, the oxygenated Ti compounds and their hydrates were dehydrated. At the same time, the incompletely oxidized TiH_2 and the oxygen compounds on the particle surface participated in ion diffusion-exchange reactions in the interface, resulting in the formation of Ti^{3+} and Ov [22]. Because the degree of surface oxidation of the yellow gel was higher than that of the green gel, its content of TiH_2 was lower, so pure anatase phase Ti^{3+} self-doped TiO_2 nanoparticles were obtained after only a short hydrothermal treatment time. Compared with the use of tetrabutyl titanate as the raw material to prepare TiO_2 containing surface Ti^{3+} [35,36], our adoption of a low valent titanium compound as the raw material means that during the initial stage of the reaction, the Ti^{2+} ions located on the particle are converted to TiO_2 contains Ti^{3+} in both the lattice and surface through ion diffusion and exchange reactions, which ensures the stability of the material. Meanwhile, using H_2O_2 as an oxidant can guarantee the purity of the product, and controlling the degree of oxidation of TiH_2 and the subsequent hydrothermal treatment conditions allows the content of Ti^{3+} and Ov in the final products to be controlled to adjust their catalytic performance.

3.5. Photocatalytic activity and reaction mechanism

MB is a brightly colored blue cationic thiazine dye often used as a test model pollutant in semiconductor photocatalysis. Fig. 6(a) illustrates the ability of the Ti^{3+} self-doped TiO_2 nanoparticles samples to photodegrade MB solutions in comparison with that of p- TiO_2 . Before illumination, all samples exhibited a certain MB absorption, among which the sample obtained from the yellow gel precursor after 20 h hydrothermal treatment had the best adsorbability. This is because the shorter hydrothermal treatment time meant that the sample size was smaller and the specific surface area was larger. The adsorption properties of the samples decreased gradually with increasing hydrothermal treatment time, owing to larger particle sizes and smaller specific surface area, consistent with the TEM results. Sample Y-24 showed the best photocatalytic performance, followed by sample G-32. Although samples Y-20 and G-27 exhibited strong absorption in visible light region, their catalytic performance was not very good compared with that of Y-24 and G-32. First, incompletely reacted TiH_2 in these samples caused their absorption in the visible light. Second, the poor crystallinity of Y-20 and G-27 meant that there were more internal defects in the particles, which acted as recombination centers for electrons and holes, decreasing the photocatalytic performance. Comparatively, the hydrothermal treatment time of sample Y-24 was short, the particle size was small, and the specific surface area was large, making it good for photocatalytic reaction. Moreover, the XPS and ESR results showed that the content of Ti^{3+} and Ov was higher when the hydrothermal treatment time was shorter; high concentrations of Ti^{3+} and Ov

Fig. 6. (a) Photodegradation of MB solutions using p-TiO₂ and obtained samples under visible light irradiation; (b) Kinetic study of photocatalytic oxidation of MB monitored using $\ln(C_0/C)$ versus irradiation time; (c) Recycling test results for samples Y-24 and G-32; (d) Schematic illustration of electron transition caused by visible light irradiation and photocatalytic process of Ti³⁺ self-doped TiO₂.

enhanced the visible light response, so the photocatalytic activity of sample Y-24 was the best among these samples.

The photocatalytic activity of the powders can be quantitatively evaluated by comparing their apparent reaction rate constants using the Langmuir–Hinshelwood equation $K_{app} = \ln(C_0/C)/t$ to calculate the photocatalytic reaction rate, where K_{app} is the first order reaction rate constant. K_{app} was obtained from the linear time dependences of $\ln(C/C_0)$, as shown in Fig. 6(b). Under visible light irradiation, the rate constants for MB degradation followed the sequence Y-24 > G-32 > Y-20 > G-27 > p-TiO₂. Sample Y-24 exhibited a first-order rate constant of $K_{app} = 0.0439 \text{ min}^{-1}$, about 18.3 times greater than that of p-TiO₂ under visible light irradiation.

The stability of a photocatalyst is highly important to its application. The cyclic stability of samples Y-24 and G-32 were examined, and the results showed the maintenance of an excellent photocatalytic activity for degrading MB solution, as shown in Fig. 6(c). After 8 reuses, the photocatalytic degradation efficiency of the samples was over 95%, which illustrated that the samples had good stability and good potential for prac-

tical application.

The introduction of Ti³⁺ or O_v in TiO₂ can form a local state at the bottom of the conduction band (CB) in the range of 0.75–1.18 eV, so that the TiO₂ has visible and infrared absorptions. When the content of Ti³⁺ and O_v reaches a certain concentration, the local state can form a similar doping energy level, thereby reducing the width of the forbidden band of TiO₂ [17]. During visible light excitation, electrons can transit from the valence band (VB) of TiO₂ to the local state formed by Ti³⁺ and O_v, and then transit to the CB, so that TiO₂ can be excited by visible light and even infrared light [10,20,36]. It is reported that defects, especially lattice defects, increase the probability of the recombination of photogenerated electron and holes, thereby reducing the photocatalytic activity [37]. As a kind of defect, Ti³⁺, on the one hand, acting as an electron capture agent, can increase the electrical conductivity of the photocatalyst and accelerate the transfer of electrons and holes [38]. On the other hand, the synergistic effect of Ti³⁺ and O_v can prolong the life time of electrons and holes, reducing the recombination rate [11,28,39,40]. Figure 6(d) shows a schematic diagram of

Graphical Abstract

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Preparation of Ti^{3+} self-doped TiO_2 nanoparticles and their visible light photocatalytic activity

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Ti^{3+} self-doped TiO_2 nanoparticles were synthesized by hydrothermal treatment of gels of different states obtained using TiH_2 and H_2O_2 . The samples showed excellent visible light photocatalytic activity.

the visible light photocatalytic reaction mechanism of the Ti^{3+} self-doped TiO_2 nanoparticles. Upon excitation with visible light, electrons transit from the VB of TiO_2 to the local state, leaving a hole in the VB. The electrons in the local state can continue to the CB of TiO_2 . The hole in the VB is captured by $-\text{OH}$ and H_2O to form $\bullet\text{OH}$, and the electrons in the local state and CB react with the O_2 molecules dissolved in the water to form superoxide radical anions ($\text{O}_2^{\bullet-}$). These $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$ species are able to degrade the MB molecules in solution. Meanwhile, the photogenerated holes also have strong oxidation ability and can directly degrade MB, thereby contributing to the high visible light photocatalytic activity.

4. Conclusions

In summary, Ti^{3+} self-doped TiO_2 nanoparticles were synthesized by mild hydrothermal treatment of two different gel precursors obtained by controlling the oxidation of TiH_2 in H_2O_2 solution. The presence of Ti^{3+} and Ov gave the resulting TiO_2 an obvious absorption in the visible region. For otherwise identical hydrothermal treatment conditions, the state of the precursor gel and subsequent hydrothermal treatment time can affect the contents of Ti^{3+} and Ov in the product. TiO_2 nanoparticles with different Ti^{3+} and Ov content were therefore obtained by controlling the preparation method, allowing control of their photoelectric conversion performance. The products obtained through hydrothermal treatment of the yellow gel had regular morphology and uniform particle size distribution, and a high content of Ti^{3+} and Ov. The photocatalytic results indicated that the samples were relatively stable.

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Ti³⁺自掺杂的纳米TiO₂的制备及其可见光催化性能

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摘要: 以TiH₂为Ti源, H₂O₂为氧化剂, 首先通过表面氧化得到不同状态的前驱体凝胶, 然后采用后续水热处理制备Ti³⁺自掺杂的纳米TiO₂. 考察了前驱体凝胶状态及水热处理时间对材料结构和性能的影响. 利用X射线衍射、透射电子显微镜、X射线光电子能谱、电子顺磁共振波谱和紫外-可见漫反射光谱手段对样品进行表征. 以次甲基蓝溶液为模拟废水评价样品的可见光催化降解性能. 结果表明, 与纯TiO₂相比, Ti³⁺的自掺杂使材料在可见光区有明显的吸收, 并具有良好的可见光催化降解性能和循环使用性能. 当采用黄色凝胶为前驱体时, 在160 °C下水热处理24 h所得样品在可见光下光催化降解次甲基蓝的反应速率常数(0.0439 min⁻¹)是纯TiO₂的18.3倍.

关键词: Ti³⁺自掺杂; 二氧化钛; 凝胶; 水热法; 可见光催化

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1. 前言

TiO₂具有无毒、光化学稳定等优点, 是最有前途的半导体光电转换材料之一^[1]. 然而, 锐钛矿相TiO₂的禁带宽度为3.2 eV, 光吸收仅限于不到太阳光5%的紫外区, 因此如何充分利用占太阳光43%的可见光部分来提高TiO₂的光电转换性能显得尤为重要. 虽然用离子掺杂、贵金属修饰、表面等离子体增强吸收、有机染料光敏化、半导体复合等方法来解决TiO₂在可见光区无吸收的问题, 然而并没有从根本上解决其光电转换效率低的问题^[2-7]. 另一方面, 纯的TiO₂电子迁移率低(0.1⁻⁴ cm²·V·s⁻¹), 大量光生电子和空穴在颗粒内部的晶格缺陷和由掺杂引起的杂质缺陷部位复合, 从而使总体光电效率不高^[8,9]. 因此, 设计能够被可见光激发并具有快速光生电子传输的

TiO₂一直是一个热点问题.

研究表明, Ti³⁺自掺杂的TiO₂能够被可见光激发^[10], 同时使TiO₂具有良好的电子导电性, 这对提高TiO₂的光电转换效率非常重要^[11,12]. 但从电极电势考虑, 在通常的条件下, 将Ti⁴⁺还原为Ti³⁺是困难的, 而且产生的Ti³⁺非常容易氧化成Ti⁴⁺^[13,14]. 目前制备Ti³⁺自掺杂TiO₂的方法大都是基于“还原法”, 在真空或强还原性气氛如H₂, CO中加热TiO₂, 或采用高能粒子(电子、氩离子)轰击^[15-17]. 在实际应用中, 这些方法有一定的局限性, 如步骤多、条件苛刻、反应时间长和设备昂贵等. 而且, 还原法反应通常发生在颗粒的表面, 形成的Ti³⁺很容易被空气和水中的溶解O₂氧化, 降低材料的稳定性^[14]. 虽然在温和的液相中还原Ti⁴⁺可用于制备Ti³⁺掺杂的TiO₂, 但是由于反应过程中有副产物生成, 需要进行后续处理才能得到纯的

Ti^{3+} 自掺杂 TiO_2 ^[18,19]. 因此,设计一种简单、经济的 Ti^{3+} 自掺杂纳米 TiO_2 的制备仍然是个挑战.

根据电极电势可知($\text{Ti}^{3+} \rightarrow \text{Ti}^{2+}$, $\varphi_{\text{A}}^0 = -0.37 \text{ V}$), Ti^{2+} 很容易被氧化成 Ti^{3+} , 因此,我们以对水、空气稳定的工业原料 TiH_2 为 Ti 源,采用“氧化法”在水相中制备 Ti^{3+} 自掺杂 TiO_2 纳米结构. 用 TiH_2 为原料具有独特的优势,即通过控制 Ti^{2+} 到 Ti^{3+} 的氧化,将 Ti^{3+} 掺杂到 TiO_2 中,完全避免采用 H_2 或 CO 还原 Ti^{4+} 到 Ti^{3+} 所需用的苛刻的实验条件和长的反应时间^[20,21].

在前期研究中,我们采用 H_2O_2 氧化 TiH_2 得到黄绿色前驱体凝胶,然后进行不同方式的后处理得到 Ti^{3+} 自掺杂的纳米 TiO_2 ^[22]. 在凝胶制备过程中没有考虑 H_2O_2 用量、氧化时间等因素. 众所周知, Ti^{4+} 与 H_2O_2 反应会得到不同组成的配离子,因此在凝胶制备过程中 H_2O_2 的用量、氧化时间等参数会影响在 TiH_2 颗粒表面生成的 Ti 的含氧化合物的种类和数量,从而影响最终产品的性能. 因此本文通过控制 H_2O_2 的加入量和氧化时间,分别得到两种不同状态的前驱体凝胶,进而对凝胶进行水热处理,研究不同状态的前驱体凝胶对最终产品的影响. 采用X射线衍射(XRD)、透射电镜(TEM)、高分辨透射电镜(HRTEM)、X射线光电子能谱(XPS)、电子自旋共振谱(ESR)、紫外-可见漫反射光谱(UV-Vis DRS)对产物的结构、形貌、 Ti 的存在状态和光学性能进行表征,并以次甲基蓝(MB)溶液为模拟废水,考察样品的可见光催化性能.

2. 实验部分

2.1. 催化剂制备

前驱体凝胶的制备流程与文献[20]类似,不同的是本文通过控制 H_2O_2 的加入量和氧化时间,分别得到黄色凝胶和绿色凝胶前驱体,然后转移到内衬聚四氟乙烯的反应釜中,在 160°C 下水热处理不同时间. 反应完成后,自然冷却到室温,过滤、洗涤、烘干后即得到蓝灰色到浅蓝色产物. 其中黄色凝胶所得产物标记为Y-t,绿色凝胶所得产物标记为G-t, t表示水热处理时间(h). 为了比较,本文还以 TiCl_4 为 Ti 源,采用水热法,在 160°C 下反应24 h制备了纯的 TiO_2 (标记为p- TiO_2).

2.2. 催化剂表征

物相组成表征在Rigaku DMax-2500型X-射线衍射仪上进行, $\text{Cu K}\alpha$ ($\lambda = 0.15418 \text{ nm}$)辐射,石墨单色器,扫描速度 $0.02^\circ/\text{min}$. 通过Hitachi H-800和JEOL JEM-2100型TEM观测材料的形貌和结构,测试时加速电压 150 kV ,测

试前样品在无水乙醇中超声分散5–10 min,然后取悬浮液滴在附有碳膜的铜网上,干燥后进行观察. 用ESCA 3000型X射线光电子能谱仪进行样品的表面成分和价态分析, $\text{Al K}\alpha$ ($h\nu = 1486.6 \text{ eV}$)为辐射源. 采用FA-200型电子顺磁共振波谱仪在室温下进行ESR测试. 在岛津UV-2550型紫外-可见吸收光谱仪上测量UV-Vis-DRS光谱,以标准 BaSO_4 为参比.

2.3. 催化性能评价

采用可见光下对MB溶液的降解来评价材料的性能,光源采用带有 400 nm 滤波片的PLS-SXE300型氙灯(北京泊菲莱科技有限公司). 将 60 mg 催化剂加入到 100 mL MB溶液($2 \times 10^{-5} \text{ mol/L}$)中,首先在暗处搅拌30 min,使MB在催化剂表面达到吸-脱平衡,然后保持催化剂悬浮状态,开启光源进行光催化降解实验,光源与溶液的距离为 30 cm . 每间隔10 min,吸取约 3 mL 上层溶液进行高速离心分离,用UV-7200型分光光度计在MB的最大吸收波长处测定上层清液的吸光度.

3. 结果与讨论

3.1. XRD物相分析

采用XRD表征产物的物相和结晶性,图1为不同状态前驱体凝胶在 160°C 下水热处理不同时间所得产物的XRD谱. 可以看出,在水热处理时间为20 h时,由黄色凝胶经水热处理后所得产物中 TiH_2 的含量很低,除了在 $2\theta = 34.9^\circ$ 和 40.6° 处出现两个微弱的 TiH_2 的衍射峰之外(图1, JCPDS 65-0934),只观察到锐钛矿相 TiO_2 的衍射峰(JCPDS 21-1272). 而以绿色凝胶为前驱体所得产物中 TiH_2 的含量很高. 进一步延长水热处理时间时,黄色凝胶前驱体经24 h水热处理即得到纯的锐钛矿相 TiO_2 ,黄绿色凝胶经27 h完全转化为 TiO_2 ^[22],而绿色凝胶经水热处理27 h后仍含有少量 TiH_2 ,只有延长至32 h后才得到纯的锐钛矿相 TiO_2 .

在 H_2O_2 存在下,随体系的酸碱条件不同, Ti^{4+} 显现不同的颜色,在酸性条件时为橙色,pH~8时为黄色,强碱性条件时为无色. 而本文在凝胶的制备过程中始终保持反应体系的pH为中性,因此所得不同状态的凝胶是由于 H_2O_2 对 TiH_2 的氧化程度不同、凝胶中 Ti 的含氧化合物和 TiH_2 的比例不同造成的. 在相同的水热处理条件下,由黄色凝胶得到的产物中 TiH_2 的含量低,说明它被氧化的程度大,同时在水热处理过程中更易完全转化为 TiO_2 ;而绿色凝胶中 TiH_2 被氧化的程度小, TiH_2 含量高,需要较长的水热处理时间才能转化为 TiO_2 . 另外,无论以哪种状态

的凝胶为前驱体,随水热处理时间的延长, TiO_2 的衍射峰越来越尖锐,说明 TiO_2 的结晶性越来越好,晶粒度越来越大.因此,在以 TiH_2 为Ti源,以 H_2O_2 为氧化剂制备凝胶前驱体并采用水热处理制备 Ti^{3+} 自掺杂的纳米 TiO_2 时,可以通过控制氧化时间和氧化程度,得到黄色凝胶,从而缩短水热处理时间.

3.2. TEM结果

图2为不同状态前驱体凝胶在 160°C 下水热处理不同时间所得产物的TEM和HRTEM照片.可以看出,黄色凝胶前驱体在 160°C 下水热处理20 h所得产物为分散较好的小颗粒组成(图1(a)),但由于样品中 TiH_2 的含量非常少,因此在其HRTEM照片中没能发现 TiH_2 的晶格结构.当水热处理时间延长到24 h后,样品形貌变得更加规则,而且分散性得到改善(图1(b)),XRD结果表明,此时样品为纯的锐钛矿相 TiO_2 (图1, Y-24).而在相同的条件下,由绿色凝胶经水热处理20 h所得产物形貌不规则,粒度分布范围较宽(图1(c)),HRTEM结果表明,样品中仍有 TiH_2 ,图2(d)中 $d=0.44\text{ nm}$ 为 TiH_2 ^[23].这进一步说明采用绿色凝胶作为前驱体进行水热处理时,在较短的时间内得到的产物为未完全转化的 TiH_2 和 TiO_2 的复合物.随水热处理时间的延长,样品的形貌越来越规则,至32 h时,由绿色凝胶所得产物的分散较好、具有一定形貌的颗粒(图1(e)),且为纯的锐钛矿相 TiO_2 (图2(f)),与XRD结果一致.比较由不同状态的前驱体凝胶全部转化为 TiO_2 后的结果可知,采用黄色凝胶所得产物的粒度最小,而采用绿色凝胶所得产物的粒度最大(图2(b),(e)).对非均相光催化反应来说,催化剂的粒度越小,则比表面积越大,样品的分散性好,吸附性强,催化剂更容易分散并与溶液中的有机分子接触,从而有利于光催化反应的进行^[24].

3.3. XPS和ESR结果

为了确定样品的组成和Ti的状态,对样品进行了XPS和ESR分析.图3(a)和(b)分别给出了样品Y-20, Y-24和G-32的Ti 2p和O 1s高分辨XPS谱.图3c, d分别是样品G-32和Y-24的Ti 2p与O 1s的拟合结果. Ti^{4+} 的2p结合能位于 ~ 464.5 和 $\sim 459.0\text{ eV}$ 处^[25],而样品Y-20和Y-24的 Ti^{4+} 结合能都向低能方向移动,这是因为样品中存在 Ti^{3+} 所致^[17].随水热处理时间的延长,向低能方向移动的程度减小,说明样品中 Ti^{3+} 的浓度降低.对样品G-32的Ti 2p结合能进行拟合后得到四个峰(图3(c)),分别为在 457.7 eV 处的 $\text{Ti}^{3+} 2p_{3/2}$, 458.7 eV 处的 $\text{Ti}^{4+} 2p_{3/2}$, 463.0 eV 处的 $\text{Ti}^{3+} 2p_{1/2}$ 和 464.5 eV 处的 $\text{Ti}^{4+} 2p_{1/2}$ ^[25,26],但是 Ti^{3+} 的结合能峰强度很弱,说明在 160°C 下水热处理32 h后样品中 Ti^{3+} 的含

量低.

Ti-O键中O的结合能位于 $529.5\text{--}530.5\text{ eV}$ 处^[27].图3b是样品的O 1s高分辨XPS谱,三个样品的O结合能都处在 530 eV 左右,说明样品中O主要以Ti-O键的形式存在,但是O结合能峰不对称.对样品Y-24的O结合能进行拟合后得到三个峰(图3(d)),其中位于 530.1 eV 处的谱峰对应于Ti-O,而 531.3 eV 处的峰对应表面氧缺陷即Ov^[28],另外在 532.3 eV 处还存在一个微弱的峰,这对应于-OH中O的结合能特征峰^[29,30],说明颗粒表面存在-OH.

ESR被用来研究物质中未耦合电子及它们与周围原子的相互作用,而且从峰的强度还可进行定量分析.图4为样品Y-20, Y-24, G-27和G-32以及纯 TiO_2 的ESR谱.与纯 TiO_2 相比,采用不同凝胶前驱体进行水热处理所得样品中,都在 $g=1.94$ 左右都出现一个信号峰,这对应于 Ti^{3+} 的信号峰.随水热处理时间的延长,该峰强度降低,说明样品中 Ti^{3+} 的浓度随水热处理时间的延长而下降^[31],和XPS结果一致.而作为电子陷阱的Ov在 $g=2.003$ 左右产生信号峰,表明样品中存在表面 Ti^{3+} ^[32],从而说明样品中的 Ti^{3+} 既存在于晶格内部,也存在于表面.样品中 Ti^{3+} 和Ov的量都随水热处理时间的延长而逐渐降低,与XPS结果一致.

XPS和ESR结果表明,不同氧化程度的凝胶前驱体经水热处理后所得样品中含有晶格 Ti^{3+} 、表面 Ti^{3+} 和Ov,这些 Ti^{3+} 和Ov的存在对其光电转换性能有重要影响,而样品表面的-OH基团能够捕获空穴形成重要的氧化性羟基自由基($\cdot\text{OH}$),这对有机污染物分子的光降解具有重要作用^[33,34].

3.4. 催化剂的光吸收性能

图5为p- TiO_2 与不同条件下所得样品的UV-Vis DRS谱.与p- TiO_2 相比,不同条件下所得样品在可见光区都有一定的吸收.其中Y-20和G-27样品虽然在可见光区的吸收较强,但是其在紫外光区的吸收弱.这是由于样品中有未完全反应的 TiH_2 引起的;另一方面,由于水热处理时间较短,样品结晶性差、缺陷较多导致的.无论是采用黄色凝胶还是绿色凝胶作为前驱体,所得样品在紫外光区的吸收都随水热处理时间的延长而增强.这是因为样品的结晶性越来越好,缺陷越来越少所致.另外,无论是在可见光区还是紫外光区,样品Y-24和G-32都有强的吸收,这说明样品结晶性好,缺陷少,同时样品中存在 Ti^{3+} .但是在可见光区,样品Y-24的吸收强于样品G-32,这说明Y-24样品中 Ti^{3+} 的浓度比G-32中的高,这也与XPS和ESR结果一致.

结合以上结果我们认为,在 H_2O_2 的氧化作用下, TiH_2 颗粒表面的 Ti^{2+} 逐渐被氧化,并且在颗粒表面形成Ti的含氧化合物及其水合物.当对前驱体凝胶进行水热处理时,表面的Ti的含氧化合物及其水合物发生脱水反应,同时颗粒内部未完全被氧化的 TiH_2 和表面Ti的含氧化合物在界面处发生离子扩散与交换反应,从而形成 Ti^{3+} 和 $\text{Ov}^{[22]}$.由于黄色凝胶比绿色凝胶表面被氧化的程度大, TiH_2 含量低,所以在较短的水热处理时间下即可得到纯锐钛矿相 Ti^{3+} 自掺杂纳米 TiO_2 .与通常采用的以四价钛醇盐为原料制备含有表面 Ti^{3+} 的 TiO_2 相比^[35,36],我们采用的原料为低价钛的化合物 TiH_2 ,在制备过程中,在反应初期 Ti^{2+} 离子位于颗粒的内核,然后通过离子扩散与交换反应得到 TiO_2 晶格内部含有 Ti^{3+} 的 TiO_2 ,这保证了材料的稳定性;同时采用 H_2O_2 为氧化剂,可以保证所得产物的纯净性,而且可以通过控制 H_2O_2 对 TiH_2 的氧化程度及后续的水热处理条件,调控最终产物中 Ti^{3+} 和 Ov 的量,进而调节产物的性能.

3.5. 光催化反应活性及反应机理

作为一种偶氮类染料,MB溶液常用来作为光催化降解的模拟废水.本文在可见光下对MB溶液的光催化降解性能和循环使用性能,结果见图6.可以看出,在打开光源前,样品都具有一定的吸附性能,其中以黄色凝胶为前驱体经水热处理20 h所得样品的吸附性能最好.这是因为水热处理时间短,样品的粒度小、比表面积较大引起的,随水热处理时间的延长,样品的吸附性能逐渐下降,这是因为样品的粒度越来越大,比表面积越来越小造成的.当打开光源进行光照时,采用黄色凝胶、在 160°C 下水热处理24 h所得样品的催化性能最好,其次是样品G-32.虽然样品Y-20和G-27在可见光区的吸收较强,但其催化性能不是很好.这是因为样品中含有未完全反应的 TiH_2 导致的在可见光区的吸收;另一方面,样品的结晶性较差,颗粒内部含有较多的缺陷,这些缺陷会成为光生电子和空穴的复合中心,因此其光催化性能相对较差.与G-32相比,样品Y-24水热处理时间短,粒径小,比表面积大,有利于光催化反应的进行;同时从XPS和ESR结果可知,在较短的水热处理时间下样品中 Ti^{3+} 和 Ov 的含量较高,对可见光的响应强,因此样品Y-24的光催化性能最好.

进一步采用准一级动力学反应方程式 $K_{\text{app}} = \ln(C_0/C)/t$ 计算光催化反应速率, K_{app} 是表观一级反应速率常数,图6(b)给出了不同条件下所得样品及p- TiO_2 在达到吸附平衡后光催化降解MB的反应动力学曲线.可以

看出,样品的催化活性从高到低的次序为 $\text{Y-24} > \text{G-32} > \text{Y-20} > \text{G-27} > \text{p-TiO}_2$,其中样品Y-24的光催化速率常数为 0.0439 min^{-1} ,是p- TiO_2 的18.3倍.

对催化剂来说,材料的耐久性是一个重要指标,对材料的重复使用可证明材料具有耐久性.图6(c)是样品Y-24和G-32的循环使用性能.可以看出,随使用次数的增加,样品的催化性能有所下降,但使用8次后其催化性能仍能达到95%左右,说明样品有较好的实际应用前景.

已有研究表明, Ti^{3+} 和 Ov 能够在 TiO_2 导带(CB)下方的 $0.75\text{--}1.18 \text{ eV}$ 范围内形成局域态,当 Ti^{3+} 和 Ov 达到一定浓度时,这种局域态类似形成掺杂能级,从而降低 TiO_2 的禁带宽度^[17].在可见光激发下,电子可以从 TiO_2 的价带跃迁至由 Ti^{3+} 和 Ov 形成的局域态中,然后从局域态再跃迁至导带,从而使 TiO_2 能够被可见光甚至红外光激发^[10,20,36].虽然 Ti^{3+} 自掺杂的纳米 TiO_2 有很多 Ov 和 Ti^{3+} 缺陷,而有研究表明, TiO_2 中的缺陷特别是体相缺陷的增加会导致光生电子和空穴的复合几率增加,从而降低光催化活性^[37].但是,由于 Ti^{3+} 的掺杂能够降低 TiO_2 的电阻,加速电子的传输^[38];同时由于 Ov 和 Ti^{3+} 的协同作用,能够延长光生载流子的寿命,降低复合几率^[11,28,39,40].图6(d)给出了 Ti^{3+} 自掺杂的纳米 TiO_2 可见光催化反应机理示意图.在可见光激发下,电子从 TiO_2 的价带(VB)跃迁至局域态中,在VB中留下空穴,处于局域态中的电子可以继续跃迁至 TiO_2 的CB中.处于VB中的空穴被催化剂表面的 $-\text{OH}$ 和溶液中的 H_2O 分子捕获形成 $\cdot\text{OH}$,而处于局域态和CB中的光生电子和水中溶解的 O_2 分子形成超氧自由基负离子($\text{O}_2\cdot^-$), $\cdot\text{OH}$ 和 $\text{O}_2\cdot^-$ 都能将溶液中的MB分子降解;同时,光生空穴也具有强的氧化能力,能够直接将MB分子催化降解,从而使表现出良好的可见光催化活性.

4. 结论

利用 TiH_2 为钛源,通过控制 Ti^{2+} 到 Ti^{3+} 的氧化,制备得到含有晶格和表面 Ti^{3+} 的纳米 TiO_2 , Ti^{3+} 和 Ov 的存在使 TiO_2 在可见光区有明显的吸收.在相同的水热处理条件下,前驱体凝胶状态及后续水热处理时间都影响产物中 Ti^{3+} 和 Ov 的含量.因此可以通过控制制备方法,得到不同 Ti^{3+} 和 Ov 含量的 TiO_2 纳米材料,从而调控 TiO_2 的光电转换性能.由黄色凝胶经水热处理后所得产物形貌规则,粒度分布较均匀,而且 Ti^{3+} 和 Ov 的含量高.光催化结果表明,样品具有相对稳定的循环使用性能,说明样品中的 Ti^{3+} 能稳定存在.