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Article

Ti³⁺ and carbon co-doped TiO₂ with improved visible light photocatalytic activity

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ABSTRACT

Using ethanol as the carbon source, a series of Ti³⁺ and carbon co-doped TiO₂ samples were successfully synthesized by an innovative and simple vacuum activation method in a one-step process. The Ti³⁺ self-doped TiO₂ featured a high visible light photocatalytic activity that improved considerably following subsequent carbon doping modification of the catalyst surface. The samples were characterized by X-ray diffraction, UV-Vis diffuse reflectance spectroscopy, electron spin resonance, X-ray photoelectron spectroscopy, and Fourier transform infrared spectroscopy. The Ti³⁺ and C co-doped TiO₂ catalyst showed a high methyl orange photo-degradation efficiency under visible light irradiation. The doping levels induced by Ti³⁺ and oxygen vacancies were responsible for the improved visible light response of TiO₂. Simultaneously, the surface coverage of graphite on the catalyst could improve the absorption of visible light and migration efficiency of photo-induced electrons. The synergistic effects of Ti³⁺ self-doping and graphite coverage led to the improved visible light photocatalytic activity of Ti³⁺ and C co-doped TiO₂.

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1. Introduction

As an environmentally friendly catalyst, TiO₂ is gaining increasing attention because of its non-toxicity, photo-chemical stability, and low cost [1,2]. However, the energy bandgap of TiO₂ is in the range of 3.0–3.2 eV that can only afford ultraviolet photocatalytic activity. Moreover, sunlight only comprises 3%–5% ultraviolet light. As a result, modification of TiO₂ towards improvement of its visible light photocatalytic activity as well as indoor light photocatalytic activity is becoming a hot research area. The surface morphology of TiO₂, especially the surface chemical state, is closely related to the photocatalytic

activity. Hence, modification of TiO₂ via Ti³⁺ doping and introduction of surface oxygen defects states have attracted increasing attention recently. Sasikala et al. [3] demonstrated that abundant Ti³⁺ and oxygen vacancies on the surface of TiO₂-SnO₂ photocatalyst were responsible for the light absorption in the visible light region. Lu et al. [4] used a high-temperature calcination method to produce many oxygen defects on the surface of TiO₂(001) facet. They showed that each oxygen defect had two neighboring Ti³⁺ ions. The Ti³⁺ ions could easily react with the adsorbed D₂O, ¹³CH₂O, and ¹⁵NO on the surface of the catalyst. Detecting the reduction products could afford quantitative measurements of Ti³⁺ species and oxygen defect

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states. Zuo et al. [5] adopted a one-step chemical reduction method to obtain reduced TiO_2 with stable Ti^{3+} that successfully induced photo-splitting of water for H_2 production. Although there are many research studies conducted on Ti^{3+} and oxygen vacancies in TiO_2 , their formation mechanism is still controversial. Guo et al. [6] investigated the transformation of the $\text{TiO}_2(110)$ surface from the (1×1) form to a (1×2) structure using electron-stimulated desorption ion-angular distribution in association with low-energy electron diffraction. They found that the bridging oxygen was easier to escape than the in-plane oxygen. The pattern of the O^+ ion emission normal to the surface from a (1×1) surface changes to two off-normal lobes upon transformation to (1×2) , reflecting a distinct change in the bonding configuration of the oxygen anion species at the surface. The result provides strong evidence for the formation of oxygen vacancies. Fischer et al. [7] showed that in addition to the bridging oxygen, the interstitial Ti^{3+} on the sub-surface of TiO_2 participated in the reaction processes relating to the surface morphology of TiO_2 . The transfer of interstitial Ti instigated a more complex formation process of reduced Ti^{3+} on the surface of TiO_2 . Hence, we can infer that the formation of Ti^{3+} cannot result from the departing oxygen atoms, which is always accompanied by the generation of oxygen vacancies.

On the other hand, considering the poor thermal stability of doping metal ions and electron-hole recombination centers induced by excess doping amounts of metal ions, co-doping with a nonmetallic ion is a good strategy to overcome these issues. Irie et al. [8] prepared carbon-doped TiO_2 (C- TiO_2) by heating TiC in air. X-ray diffraction (XRD) analysis confirmed that the oxygen in TiO_2 lattice was substituted by carbon. The C- TiO_2 sample displayed a high visible light photocatalytic activity with a quantum yield of 0.2%. Lettmann et al. [9] adopted a one-step sol-gel method to fabricate C- TiO_2 using a different alkoxide as precursor. A surface-carbonized TiO_2 was obtained following calcination, and featured a large specific surface area. A high amount of coke deposited on the catalyst surface afforded photo-sensitization of the catalyst, consequently leading to the high degradation rate of 4-chlorophenol under visible light irradiation. In our previous work, carbon was co-doped with La to improve the photocatalytic activity of TiO_2 [10]. The synergistic effect between C and La played an important role in the photo-degradation of methyl orange (MO) and salicylic acid. Hence, carbon is an ideal co-dopant to further improve the visible light photocatalytic activity of TiO_2 .

Herein, ethanol was used as the carbon source and a hydrothermal method was adopted to synthesize C-doped TiO_2 . Then, a simple vacuum activation method was used to prepare Ti^{3+} and C co-doped TiO_2 . All the prepared catalysts featured high visible light photocatalytic activity towards the degradation of MO. The co-doped catalysts displayed enhanced photoactivity. The synergistic effect between the Ti^{3+} and C species was also investigated to illustrate the high photoactivity of the co-doped catalysts.

2. Experimental

2.1. Materials and synthesis

P25 was purchased from Degussa. Other chemicals were of analytical reagent grade and used without further purification. Experimental solutions were prepared with doubly distilled water.

First, 0.5 g P25 was placed in a vacuum tube furnace for vacuum calcination at different temperatures for 3 h. The resulting Ti^{3+} -doped TiO_2 samples are denoted as V-P25- n ($n = 1, 2, 3, 4$, and 5 represents the calcination temperature at 100, 200, 300, 400, and 500 °C, respectively).

First, 0.5 g P25, 40 mL water, and ethanol (at a certain amount) were mixed and stirred for 2 h. Then, the solution was transferred to an autoclave and subjected to a hydrothermal treatment at 120 °C for 3 h. The powders were filtered, washed twice, and dried under vacuum at 60 °C for 12 h. The obtained C- TiO_2 was placed in a vacuum tube furnace for vacuum activation at 200 °C for 3 h to obtain the Ti^{3+} and carbon co-doped TiO_2 . The resulting samples are denoted as V- n C-P25 ($n = 5, 10, 20, 30$, and 40, corresponding to the amounts of added ethanol i.e., 5, 10, 20, 30, and 40 mL, respectively).

2.2. Characterization

XRD patterns of all samples were collected in the range 10° – 80° (2θ) on a Rigaku D/MAX 2550 diffractometer ($\text{Cu } K\alpha$ radiation, $\lambda = 0.15406$ nm), operating at 40 kV and 100 mA. X-ray photoelectron spectroscopy (XPS) studies were conducted on a Perkin-Elmer PHI 5000C ESCA using Al $K\alpha$ radiation operating at 250 W. The shift in the binding energy owing to relative surface charging was corrected using the C 1s peak at 284.6 eV as an internal standard. The UV-Vis absorption spectra of samples were recorded on a Varian Cary 500 equipped with an integrating sphere. The X-band electronic resonance (EPR) spectra were recorded at room temperature on a Varian E-112. To measure the amount of $\cdot\text{OH}$ radicals, 0.02 g catalyst was mixed with 20 mL benzoic acid (1 mmol/L), then irradiated under visible light for 20 min. Following filtration of the solution, the photoluminescence (PL) emission spectrum of the filtrate was recorded. Field emission scanning electron microscopy (SEM) was recorded on JEOL JSM-6360 at 15 kV. Raman spectra were recorded on Renishaw inVia+Reflex at room temperature.

2.3. Measurement of photocatalytic activity

MO is used as pollution for the test of photocatalytic activity. 0.07g catalysts were added to glass test tube and 70 mL MO solution (20 mg/L) was added after that. Visible light photocatalytic reaction was proceed in self-made device. Using iodine-tungsten lamp to mimic sunlight for the degradation ($\lambda > 420$ nm).

3. Results and discussion

3.1. Characterization of Ti^{3+} -doped TiO_2 catalysts

As observed from the XRD patterns of P25 before and after vacuum activation (Fig. 1), vacuum activation did not change

Fig. 1. XRD patterns of catalysts prepared at different vacuum activation temperatures.

the crystal structure and crystallinity of P25. The latter still featured mixed anatase and rutile phases following vacuum activation. However, the peak full width at half maximum of P25 slightly decreased with increasing activation temperatures, indicating that the particle size of P25 slight increased. Moreover, as observed from the SEM images of P25 before and after vacuum activation (Fig. 2), the microstructure of P25 remained unaltered [11]. However, the color of the TiO₂ samples changed significantly after vacuum activation from white to light brown, and is consistent with our previous results [11]. The formation of Ti³⁺ and oxygen vacancies could induce the brown coloration of P25. UV-Vis diffuse reflectance spectra in Fig. 3 also indicate that the generation of Ti³⁺ and oxygen vacancies enhances the light absorption of vacuum-activated P25 in the visible light region (400–800 nm) [12].

To further investigate the enhanced light absorption properties of the vacuum-activated catalyst in the visible light region, the Ti 2*p* and O 1*s* XPS spectra of P25 before and after vacuum activation were recorded and the results were the same as our previous work [11]. The Ti 2*p*_{3/2} characteristic peak of P25 after vacuum activation was slightly shifted, indicating the presence of Ti³⁺ species [11,13,14]. The difference in the binding energy values (6.2 eV) of the characteristic peaks Ti 2*p*_{1/2} and Ti 2*p*_{3/2} further proved the existence of Ti³⁺ [11,15]. The O 1*s* XPS peaks at 529.4 and 531.4 eV were ascribed to the Ti–O bond and chemically absorbed OH[−] on the surface of the catalyst, respectively [11,16]. Interestingly, after vacuum acti-

Fig. 2. SEM images of P25 catalyst before (a) and after (b) vacuum activation at 200 °C.

Fig. 3. UV-Vis diffuse reflectance spectra of TiO₂ catalyst before and after vacuum activation.

vation, the peak at 531.0–532.0 eV shows an obvious increase, which is due to electron transfer from the O atoms to the neighboring oxygen vacancy [11]. During the vacuum activation process, Ti³⁺ and oxygen vacancies are generated on the surface of the catalyst. These oxygen vacancies have strong electronic absorption properties, inducing a decrease in the electron cloud density of the neighboring O atom. As a result, a strong peak at a high binding energy is generated.

Figure 4 shows the EPR spectra of P25 before and after vacuum activation. No paramagnetic signals were observed for pure P25. In contrast, after vacuum activation, a strong paramagnetic signal was observed at $g = 1.988$ that is the characteristic peak of Ti³⁺ [11]. Additionally, a relatively strong paramagnetic signal at $g = 2.016$ was observed that was attributed to O_v[−], formed upon photo-induced electron capture by an oxygen vacancy [17]. Some reports have demonstrated that the presence of high concentrations of Ti³⁺ and oxygen vacancies can extend the light absorption response of TiO₂ to the visible light region [12]. Various types of Ti³⁺ and oxygen vacancies can introduce new defect levels below the conduction band of TiO₂ (0.75–1.18 eV) [18], thus increasing the light absorption of TiO₂ in the visible light region. Moreover, theoretical calculations have confirmed that oxygen defect levels (O_v⁺⁺) can be located below the conduction band when the concentration of

Fig. 4. EPR spectra of P25 before and after vacuum activation.

oxygen vacancies is sufficiently high [13]. The generation of Ti^{3+} and oxygen vacancies in P25 is expected to improve the photocatalytic activity of P25.

The photocatalytic activity of the catalysts towards the degradation of MO is shown in Fig. 5(a). Compared with non-treated P25, the vacuum-activated P25 samples showed excellent visible light photo-degradation activity towards the degradation of MO. The photocatalytic degradation efficiency initially increased with increasing activation temperatures then decreased with further increase in the activation temperature. The photo-degradation rate of MO was maximum at an activation temperature of 300 °C. The EPR spectra of the samples activated at varying temperatures are shown in Fig. 5(b). Among all samples, V-P25-3 has the highest content of Ti^{3+} that correlates to the high photoactivity of this sample. Thus, the concentration of Ti^{3+} plays an important role in improving the photocatalytic activity of the catalyst under visible light irradiation [11]. The influence of activation temperature on the concentration of Ti^{3+} is currently underway.

3.2. Characterization of Ti^{3+} and carbon co-doped TiO_2 catalyst

To further improve the photocatalytic activity of vacuum-

activated P25, carbon was used as a co-dopant to modify P25 using a one-step vacuum activation method. V-P25-2 that was obtained at a low vacuum activation temperature of 200 °C was chosen as a precursor for further modification with carbon. The XRD results (Fig. 6(a)) showed that the crystal form and crystallinity of TiO_2 remained unaltered following carbon co-doping of the P25 catalyst. Moreover, the peak full width at half maximum of TiO_2 remained unchanged with increasing amounts of carbon, suggesting that carbon may not be embedded in the TiO_2 lattice, but deposited on the surface of TiO_2 . Carbon modification on the surface did not induce lattice distortion of TiO_2 , thus the structural parameters, such as particle size, did not change.

The UV-Vis diffuse reflectance spectra (Fig. 6(b)) showed that the visible light absorption of P25 increased with increasing levels of carbon doping. V-20C-P25 catalyst that was prepared at a carbon source ethanol amount of 20 mL displayed the highest light absorption in the visible light region. However, introduction of excessive amounts of ethanol decreased the catalyst light absorption properties, especially when the amount of ethanol was higher than 20 mL. Excessive carbon species deposited on the catalyst surface masked the surface color center and decreased the absorption properties of the

Fig. 5. (a) Photocatalytic activity of non-treated P25 and P25 activated at different temperatures towards the degradation of MO; (b) EPR spectra of non-treated P25 and P25 activated at different temperatures.

Fig. 6. XRD patterns (a) and UV-Vis diffuse reflectance spectra (b) of Ti^{3+} and carbon co-doped TiO_2 catalysts with different amounts of carbon doping.

catalyst in the visible light region [19].

C 1s XPS and Raman characterization were carried out to investigate the doping form of carbon on the catalysts. As observed from the C 1s XPS spectra (Fig. 7(a)), the characteristic peak profile of C 1s remained unchanged after the co-doping modification. The peak at 284.6 eV was attributed to carbon species in the internal standard solutions, and the peak at 289.8 eV was attributed to carbon oxide species generated by the added pollutants during the test [20]. From the C 1s XPS spectra, no characteristic peaks corresponding to substitutional carbon were found in the range of 280–282 eV [21], indicating that carbon was not incorporated in the TiO₂ lattice, but instead deposited on the surface of the catalyst.

Raman spectra in Fig. 7(b) show characteristic D band and G band of graphite at 1340.5 and 1610.7 cm⁻¹, respectively [22]. The absent of characteristic peak of coke at 1400 cm⁻¹ indicates that carbon is mainly in the form of graphite deposited on the surface of TiO₂. During the vacuum activation process, the carbon species in ethanol are converted into graphite-like carbon species that can act as sensitizers to improve the photoactivity of TiO₂. In addition to the formation of graphite-like carbon species, many Ti³⁺ and oxygen vacancies are generated in TiO₂. The EPR spectra of samples before and after C co-doping are shown in Fig. 8. Further carbon co-doping modification has barely any influence on the generation of Ti³⁺, but is beneficial towards the generation of oxygen vacancies. The signal corresponding to oxygen vacancies at $g = 2.016$ was stronger following modification with carbon. This proves that the graphite carbon interacts with the oxygen on the surface of the catalyst. The co-doping of carbon does not impede the formation of Ti³⁺,

Fig. 8. EPR spectra of Ti³⁺ and carbon co-doped TiO₂.

but contributes to the generation of some carbon free radicals displaying a paramagnetic signal at $g = 2.016$. To investigate the interaction between TiO₂ and surface carbon species, the O 1s XPS spectra of the catalysts were recorded and are shown in Fig. 9(a). Relative to V-P25-2, the co-doped catalyst displayed an enhanced peak at 529.8 eV, indicating the generation of Ti–O–C bonds.

The photo-degradation of MO over the catalysts under visible light irradiation is shown in Fig. 9(b). Compared with the pure P25 and Ti³⁺-doped P25 (V-P25-2), the carbon co-doped catalysts showed higher visible light activities. The visible light photoactivity initially increased and then decreased with increasing amounts of carbon precursor ethanol added during the catalyst preparation. V-20C-P25 displayed the highest ac-

Fig. 7. (a) C 1s XPS spectra of TiO₂ catalyst before and after carbon doping modification; (b) Raman spectra of graphene (1) and V-20C-P25 (2).

Fig. 9. (a) O 1s XPS spectra of TiO₂ catalyst before and after carbon doping modification; (b) Visible light degradation of MO before and after carbon co-doping.

Fig. 10. Influence of catalyst (V-40C-P25) on the fluorescence of benzoic acid at different irradiation times.

activity among all the co-doped catalysts. Hydroxyl radicals ($\cdot\text{OH}$) are known to be the major active species during photocatalytic oxidation reactions. Some studies have reported that $\cdot\text{OH}$ species produced during photocatalysis can be detected via photoluminescence (PL) techniques [23,24]. Hence, the presence of hydroxyl radicals was evaluated accordingly, and the results are shown in Fig. 10. Benzoic acid was used as a probe to detect the formation of $\cdot\text{OH}$, owing to the formation of fluorescent hydroxybenzoic acid by $\cdot\text{OH}$ scavenging. The blank benzoic acid did not display any fluorescence. However, mixing the benzoic acid and catalyst led to an onset of fluorescence under visible light irradiation, confirming the generation of numerous hydroxyl radicals upon irradiation. Hydroxyl radicals are the main reason for the observed enhanced visible light activity.

During vacuum activation, large numbers of Ti^{3+} and oxygen vacancies are generated in TiO_2 , resulting in $\text{Ti}^{3+}\text{O}_v\text{Ti}^{3+}$ doping species located below the conduction band of TiO_2 , as shown in Fig. 11. These impurity levels can decrease the bandgap of TiO_2 and consequently improve the visible light response. On the other hand, the surface-deposited graphite-like carbon species can generate electrons under visible light irradiation that can act as sensitizers, thereby transferring the electrons to the conduction band of TiO_2 through $\text{Ti}-\text{O}-\text{C}$ bonds. This process

Fig. 11. Mechanism of photo-degradation over Ti^{3+} and carbon co-doped catalyst.

can greatly enhance the transfer efficiency of photo-generated carriers. Hence, the photo-induced electrons in the doping level and conduction band can react with O_2 to generate active species such as superoxide radicals. In contrast, the photo-generated holes in the valence band react with water to produce other active species such as hydroxyl radicals, which can photo-degrade the MO molecules to CO_2 and water. Hence, the synergistic effect between Ti^{3+} and carbon species is responsible for the high visible light photocatalytic activity of Ti^{3+} and C co-doped TiO_2 .

4. Conclusions

Ti^{3+} and carbon co-doped catalysts were successfully synthesized by a simple vacuum activation method. Vacuum activation is a useful technology for introducing Ti^{3+} and oxygen vacancies in TiO_2 . The graphite-like carbon species were deposited on the surface of TiO_2 and afforded further improvement of the visible light response and photoactivity of the catalyst. The synergistic effect of the Ti^{3+} and carbon species was responsible for the enhanced visible light photocatalytic activity of the Ti^{3+} and carbon co-doped TiO_2 catalyst.

References

- [1] He F, Ma F, Li T, Li G X. *Chin J Catal* (何霏, 马芳, 李涛, 李光兴. 催化学报), 2013, 34: 2263
- [2] Mohamed R M, Aazam E. *Chin J Catal* (催化学报), 2013, 34: 1267
- [3] Sasikala R, Shirole A, Sudarsan V, Sakuntala T, Sudakar C, Naik R, Bharadwaj S R. *Int J Hydrogen Energy*, 2009, 34: 3621
- [4] Lu G, Linsebigler A, Yates J T Jr. *J Phys Chem C*, 1994, 98: 11733
- [5] Zuo F, Wang L, Wu T, Zhang Z Y, Borchardt D, Feng P Y. *J Am Chem Soc*, 2010, 132: 11856
- [6] Guo Q, Cocks I, Williams E M. *Phys Rev Lett*, 1996, 77: 3851
- [7] Fischer S, Munz A W, Schierbaum K D, Göpel W. *Surf Sci*, 1995, 337: 17
- [8] Irie H, Watanabe Y, Hashimoto K. *Chem Lett*, 2003, 32: 772
- [9] Lettmann C, Hildenbrand K, Kisch H, Macyk W, Maier W F. *Appl Catal B*, 2001, 32: 215
- [10] Xing M Y, Qi D Y, Zhang J L, Chen F. *Chem Eur J*, 2011, 17: 11432
- [11] Xing M Y, Zhang J L, Chen F, Tian B Z. *Chem Commun*, 2011, 47: 4947
- [12] Xia T, Zhang W, Murowchick J B, Liu G, Chen X B. *Adv Energy Mater*, 2013, 3: 1516
- [13] Xing M Y, Wu Y M, Zhang J L, Chen F. *Nanoscale*, 2010, 2: 1233
- [14] Song Z, Hrbek J, Osgood R. *Nano Lett*, 2005, 5: 1327
- [15] Kim K W, Lee E H, Kim Y J, Lee M H, Kim K H, Shin D W. *J Photochem Photobiol A*, 2003, 159: 301
- [16] Li G Q, Liu C Y, Liu Y. *Appl Surf Sci*, 2006, 253: 2481
- [17] Kumar C P, Gopal N O, Wang T C, Wong M S, Ke S C. *J Phys Chem B*, 2006, 110: 5223
- [18] Cronmeyer D C. *Phys Rev*, 1959, 113: 1222
- [19] Xing M Y, Fang W Z, Nasir M, Ma Y F, Zhang J L, Anpo M. *J Catal*, 2013, 297: 236
- [20] Wu Y M, Xing M Y, Zhang J L. *J Hazard Mater*, 2011, 192: 368
- [21] Fang W Z, Xing M Y, Zhang J L. *Appl Catal B*, 2014, 160-161: 240
- [22] Zhou K F, Zhu Y H, Yang X L, Jiang X, Li C Z. *New J Chem*, 2011, 35: 353
- [23] Xing M Y, Zhang J L, Chen F. *J Phys Chem C*, 2009, 113: 12848
- [24] Xiang Q J, Yu J G, Wong P K. *J Colloid Interface Sci*, 2011, 357: 16

Graphical Abstract

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Ti³⁺ and carbon co-doped TiO₂ with improved visible light photocatalytic activityYunchang Liu, Mingyang Xing*, Jinlong Zhang*
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The synergistic effect between Ti³⁺ self-doping and graphite surface coverage is responsible for the improvement of the visible light photocatalytic activity of Ti³⁺ and carbon co-doped TiO₂ catalyst.

具有高可见光催化活性的Ti³⁺和碳共掺杂改性的TiO₂光催化剂

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摘要: 以乙醇为碳源, 采用操作简单的真空活化法一步实现对TiO₂的Ti³⁺与C的共掺杂改性, TiO₂用X衍射衍射、紫外-可见光谱、顺磁共振、X射线光电子能谱和红外光谱等手段表征了催化剂的结构、组成、光学性质。结果表明, 经Ti³⁺与C共掺杂改性后的催化剂表现出高的可见光降解甲基橙活性。复合在催化剂表面的石墨可以增强催化剂对可见光的响应范围, 而Ti³⁺与氧缺陷形成的掺杂能级则可以提高光生电子的迁移效率。实验表明, 两者之间的协同作用促进了其可见光催化活性的提高。

关键词: 真空活化法; Ti³⁺掺杂; 石墨负载; 二氧化钛; 光催化

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1. 前言

TiO₂作为一种环境友好的光催化剂, 具有无毒, 光稳定性好和价格低廉等特点, 因而备受关注^[1,2]. 然而, 其禁带宽度为3.2 eV (锐钛矿), 只有在紫外光的激发下才能表现出光催化活性. 而太阳光中紫外光的含量只占3%–5%, 因此对TiO₂进行改性, 使其在可见光甚至是室内光源的激发下产生催化活性是目前的研究热点. 由于TiO₂催化性能与其表面形态密切相关, 因此有关TiO₂表面性质一直成为研究的热点. Sasikala等^[3]研究发现TiO₂-SnO₂复合光催化剂表面存在着大量的Ti³⁺和氧空穴, 它们可能是引起催化剂在可见光区产生吸收的原因. Lu等^[4]采用真空高温煅烧的方法, 在TiO₂表面的(001)面上产生了大量的氧缺陷, 每个氧缺陷周围对应产生了两个还原态的Ti³⁺. 这些表面Ti³⁺很容易与催化剂表面吸

附的D₂O, ¹³CH₂O以及¹⁵NO发生还原反应, 对应生成D₂, ¹³C₂H₄以及¹⁵N₂O. 通过对还原产物的检测从而定量考察了表面Ti³⁺以及氧缺陷的产生情况. Zuo等^[5]采用一步化学还原反应法制备了体相中含有稳定Ti³⁺的还原态TiO₂光催化剂, 并成功用它来进行可见光解水制氢实验. Guo等^[6]采用电子激发离子解析角分布技术与低能电子衍射相结合的方法, 研究了TiO₂表面脱氧的过程. Fischer等^[7]通过对还原态TiO₂(110)面的扫描隧道显微镜(STM)研究发现, 除了桥连氧以外次表面的间隙Ti³⁺也参与了TiO₂的表面形态重组过程. 间隙Ti的迁移使得TiO₂表面还原态的产生过程变得更加复杂. 考虑到金属离子掺杂的热稳定性差, 增加了电子-空穴的复合中心, 而且掺杂的金属价格较高, 因此非金属离子的掺杂得到了越来越广泛的关注. Iire等^[8]通过加热氧化TiC粉末的方法制备C掺杂的锐钛矿型TiO₂粉末(C-TiO₂), X射线衍射

(XRD)光谱表明, C原子取代了TiO₂中O原子位置. Lettmann等^[9]以几种不同的醇盐为前驱体, 采用一种改进的溶胶-凝胶方法制备了TiO₂光催化剂. 该方法在凝胶煅烧过程中, 生成了具有大的比表面积含碳的光催化剂, 能在可见光激发下光降解4-氯苯酚. 我们曾做过碳钨共掺杂改性的光催化剂^[10], 碳钨的协同作用在光降解甲基橙和水杨酸方面起到重要作用. 因此, 碳掺杂改性是一种理想的提高二氧化钛光催化活性的方法.

本文以乙醇为碳源, 先采用水热法制备碳掺杂TiO₂, 再创新性采用真空活化法制备Ti³⁺与碳共掺杂改性TiO₂光催化剂, 考察其在可见光降解MO反应中的催化性能.

2. 实验部分

2.1. 催化剂的制备

P25购买自德国赛, 其他化学试剂均为分析纯, 且没做任何处理直接使用, 化学反应的溶液均用二次水制备.

称取0.5 g P25放置于真空管式炉中, 在不同温度下进行真空焙烧3 h, 所得样品标记为V-P25-*n* (*n* = 1, 2, 3, 4和5分别代表焙烧温度为100, 200, 300, 400和500 °C).

将0.5 g P25样品与40 mL H₂O和一定量的无水乙醇混合, 磁力搅拌2 h后, 于120 °C下水热3 h. 抽滤洗涤两次, 60 °C真空干燥, 研磨后, 将得到的样品在300 °C下进行真空活化3 h, 所得样品标记为V-*n*C-P25 (*n* = 5, 10, 20, 30和40分别代表乙醇的加入量为5, 10, 20, 30和40 mL).

2.2. 催化剂的表征

采用日本Rigaku D/max 2550 VB/PC型X射线衍射仪, 扫描范围为10°–80°. 采用弯晶石墨单色仪和Cu K_α射线, 工作电压40 kV, 电流100 mA. 采用PHI 5000C ESCA System进行X射线光电子能谱(XPS)测试, 以Al K_α射线作为激发源, 功率为250 W. 样品压片后测试, 所有结合能均以污染碳的结合能(C 1s = 284.6 eV)为基准进行校正. 采用Varian Cary 500进行紫外可见吸收(UV-Vis)光谱的测定, 自带积分球. 采用Varian E-112在室温下进行电子顺磁共振(ESR)的测试. 为了测试羟基自由基, 将0.02 g催化剂和20 mL苯甲酸溶液(1 mmol/L)混合, 在可见光下照射20 min, 抽滤进行荧光(PL)测试. 采用JEOL公司JSM-6360扫描电镜进行场发射扫描电镜(SEM)的测试, 工作电压15 kV. 拉曼光谱在Renishaw公司inVia+Reflex型光谱仪上室温下进行测量.

2.3. 光催化剂的活性测试

MO作为污染物进行光催化测试, 将0.07 g光催化剂加入玻璃试管中, 接着加入70 mL MO溶液(20 mg/L).

可见光催化测试在自制的装置上进行, 用碘钨灯模拟太阳光源进行测试($\lambda > 420$ nm).

3. 结果与讨论

3.1. Ti³⁺掺杂TiO₂光催化剂的制备及表征

图1为P25真空活化前后的XRD谱. 不难发现, 真空活化过程并不会改变P25的晶型结构和结晶度, 仍为锐钛矿和金红石的混晶. 但是, 随着活化温度的升高, P25的半峰宽略有减小, 表明其粒径略有增大. 图2为活化前后P25的SEM照片. 活化前后催化剂的微观形貌变化不大^[11]. 然而, 经过真空活化后, P25的表观颜色却发生了明显变化, 从白色变成浅棕色, 这与我们以前的工作结果是一致的^[11]. Ti³⁺和氧空穴的共同作用能够使P25着色. 图3为经过真空活化后的P25的UV-Vis谱, 可以发现其在400–800 nm可见光区范围内的吸收明显变强^[12].

真空活化前后的P25的XPS谱我们之前工作已有报道^[11]. 发现该样品活化后其Ti 2p_{3/2}特征峰的对称性明显变差, 表明有Ti³⁺的生成, 这在我们之前的工作中亦有报道^[11,13,14]. 此外, Ti 2p_{1/2}和Ti 2p_{3/2}特征峰出峰位置之差 $\Delta E = 6.2$ eV, 这也证明真空活化后P25表面出现了Ti³⁺^[11,15]. 由真空活化前后P25的O 1s的XPS谱可知, 活化前该样品在529.4和531.4 eV处分别出现Ti–O和催化剂表面化学吸附的羟基的特征峰^[11,16]; 经过真空活化后, 531.0–532.0 eV处的峰明显变强. 这并不是由于催化剂表面的羟基含量增加所致, 而是由表面的氧缺陷含量增加引起的. 图4为P25样品的EPR谱. 可以看出, 空白P25没有出现任何的顺磁信号, 而经过真空活化后则在 $g = 1.988$ 处出现了一个很强的归属为Ti³⁺的顺磁信号^[11]. 在 $g = 2.016$ 处还出现了另一个相对较强的顺磁信号峰, 这是氧缺陷捕获一个光生电子变成O_v[•]的顺磁信号峰^[17]. 已有研究指出, Ti³⁺和高浓度氧缺陷的同时出现可以使TiO₂具有强烈的可见光响应, 这主要是因为不同形态的氧缺陷和Ti³⁺可以在TiO₂导带下方0.75–1.18 eV范围内引入新的缺陷能级^[18], 从而增强其对可见光的吸收. 此外, 通过理论计算发现, 当氧缺陷的浓度足够高时, 会在导带下方产生一个单独氧缺陷能级(O_v⁺⁺).

图5(a)为真空活化前后P25在可见光下降解MO的活性图. 与空白P25相比, 经过不同温度真空活化后的P25可见光催化降解MO活性明显升高, 且随着活化温度的升高而先升后降, 至300 °C时最高. 当活化温度超过300 °C时, 催化剂的可见光催化活性大大降低. 图5(b)为不同活化温度下制备催化剂的EPR谱. 可以看出, 当活

化温度为300 °C时, 对应催化剂中 Ti^{3+} 的含量最高. 这说明 Ti^{3+} 含量对于 TiO_2 可见光催化活性起主要作用.

3.2. Ti^{3+} 与C共掺杂 TiO_2 光催化剂的表征结果

为了进一步提高真空活化P25的光催化活性, 采用一步真空活化法用C改性P25. 在低温200 °C下真空活化的V-P25-2选作前驱体, 用于C的进一步改性. 图6(a)为不同C掺杂量的 Ti^{3+} 与C共掺杂 TiO_2 的XRD谱. 由图可见, 随着C的进一步掺杂, TiO_2 的晶型和结晶度都没有发生改变, 仍为锐钛矿和金红石的混晶. 此外, 随着C掺杂量的增加, TiO_2 的半峰宽基本保持不变, 表明C并未进入 TiO_2 的晶格, 而只是存在于 TiO_2 的表面, 而表面的碳改性并未引起 TiO_2 的晶格畸变, 因而对其粒径等结构参数没有影响.

图6(b)为催化剂的UV-Vis谱. 可以看出, 随着C的进一步掺杂, 催化剂在可见光区的吸收明显增强, 当碳源乙醇的加入量为20 mL时, 对应催化剂V-20C-P25表现出最强的可见光吸收. 随着乙醇加入量的增加, Ti^{3+} 与C共掺杂催化剂在可见光区的吸收有所减弱^[19]. 图7(a)为改性前后 TiO_2 样品的C 1s XPS谱. 可以发现, C的掺杂并未使样品的C 1s的特征峰发生变化, 在284.6 eV处谱峰为XPS测试过程中内标污染的碳物种, 而289.8 eV处的则为催化剂表面由于污染所致的少量 CO_x 物种^[20]. C 1s XPS谱中并未在280–282 eV处出现晶格取代C的特征峰^[21]. 这说明C并不是以晶格取代的形式对 TiO_2 进行改性的. 图7(b)为C改性前后催化剂的Raman光谱. 与石墨相比, V-20C-P25样品在1340.5和1610.7 cm^{-1} 处出现了石墨的D带和G带特征峰^[22], 并未出现焦炭的特征峰(1400和1600 cm^{-1}), 表明以乙醇为碳源, 采用真空活化法对 TiO_2 进行改性的过程中, C主要是以石墨的形式复合在 TiO_2 的表面.

图8为碳掺杂改性前后 TiO_2 样品的EPR谱. 不难发现, C的进一步掺杂也对 Ti^{3+} 的影响不大, 但却有利于氧缺陷的产生. 随着碳的进一步改性, $g = 2.016$ 的氧缺陷的特征峰强度明显变大, 这说明在真空活化过程中, 石墨C与 TiO_2 表面的O原子之间发生了相互作用, 从而引起 TiO_2 表面晶格畸变, 促进了氧缺陷的生成. 这也说明真空活化法更有利于 TiO_2 与石墨之间的复合, 从而促进光生电荷的迁移.

图9(a)为C改性前后 TiO_2 样品的O 1s XPS谱. 与V-P25-2光催化剂相比, 随着表面碳物种的进一步复合,

V-20C-P25在529.8 eV处谱峰明显升高, 这证明有Ti–O–C键的生成. 可见, 石墨与 TiO_2 之间主要是以Ti–O–C键的方式进行键合的.

图9(b)为 Ti^{3+} 与碳共掺杂改性 TiO_2 光催化剂在可见光下降解MO的活性图. 与空白P25相比, 经过200 °C真空活化后的P25在可见光下降解MO的活性明显升高. 随着碳的进一步改性, Ti^{3+} 与C共掺杂改性的 TiO_2 表现出更高的可见光催化活性, 且随着碳的加入量的增加而先增加后降低, 当碳源乙醇的加入量为20 mL时, 对应的催化剂活性最高.

为了考察光催化过程中的活性物种, 我们以苯甲酸为探针, 检测光照过程中羟基自由基的浓度. 羟基自由基被认为是光催化过程中生成的主要活性物种, 已有文献报道, 光催化过程中生成的羟基自由基可以通过荧光检测到^[23,24]. 如图10所示, 在可见光照射下, 共掺杂催化剂产生了大量羟基自由基, 其被苯甲酸捕获产生具有荧光的对羟基苯甲酸. 随着光照时间的增加, 羟基自由基的浓度逐渐增高, 这说明羟基自由基是引起催化剂可见光活性的主要原因.

真空活化过程会使 TiO_2 的表面和体相产生大量的 Ti^{3+} 和氧空穴, 从而在 TiO_2 导带的下方产生一个 $[\text{Ti}^{3+}\text{O}_v\text{Ti}^{3+}]$ 的掺杂能级(见图11), 提高其对可见光的响应, 引起催化剂在可见光照射下产生大量光生电子和空穴. 光生电子从价带跃迁到掺杂能级, 并与氧分子作用产生超氧自由基等活性基团. 而价带上的空穴则与水分子作用生成羟基自由基等活性基团. 这些活性基团进一步与吸附在催化剂表面的染料分子发生氧化还原反应, 将染料分子降解成 CO_2 和水. 复合在 TiO_2 表面的石墨在可见光下也会产生光生电子, 并通过石墨与 TiO_2 之间形成的Ti–O–C键, 将光生电子转移到 TiO_2 的导带, 从而大大促进了光生载流子的转移效率, 有利于其可见光活性的进一步提高.

4. 结论

通过一步真空活化法成功制备出 Ti^{3+} 和C共掺杂的光催化剂, 真空活化法是一种有效的引入 Ti^{3+} 和氧空穴的方法. 类石墨的碳物种沉积在 TiO_2 表面, 并进一步提高了可见光响应和光催化活性. Ti^{3+} 与碳物种的协同作用对于提高 Ti^{3+} 和C共掺杂催化剂的光催化活性起到了主要作用.