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In situ synthesis of Ti^{3+} self-doped mesoporous TiO_2 as a durable photocatalyst for environmental remediation

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ABSTRACT

This study developed a facile approach for *in situ* synthesis of a Ti^{3+} self-doped mesoporous TiO_2 photocatalyst by an evaporation-induced self-assembly method using TiCl_3 , water, and F127 as the titanium precursor, solvent, and soft template agent, respectively. The as-prepared samples were investigated by X-ray diffraction, N_2 adsorption-desorption measurements, ultraviolet-visible diffuse reflectance spectroscopy, electron paramagnetic resonance, and transmission electron microscopy. The influence of different reaction parameters such as the dosage of F127 and calcination temperature on the photocatalytic performance of the resulting products was evaluated. The optimized product exhibited high photocatalytic activity and stability in the oxidation of nitric oxide in air and photocatalytic degradation of methylene blue. The excellent photocatalytic performance of the Ti^{3+} self-doped mesoporous TiO_2 photocatalyst is attributed to the cooperation between the mesoporous structure and self-doped Ti^{3+} enhancing light absorption and effectively suppressing the recombination of photogenerated electrons and holes.

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1. Introduction

Photocatalysis is an important type of heterogeneous catalysis that has been widely studied for environment remediation and energy production [1–4]. Among various photocatalysts, TiO_2 , the most widely studied semiconductor, has been used as an active photocatalyst in numerous applications such as water treatment [5], water splitting [6], CO_2 conversion [7], and air cleaning [8], because of its practicality and strong oxidation capacity. However, the band gap of TiO_2 is wide (about 3.2 eV), which limits its absorption range to less than 390 nm [9]. Therefore, it is crucial to enhance the light absorption of TiO_2 in the visible region. Numerous approaches to realize visi-

ble-light-driven TiO_2 have been developed. For example, the replacement of oxygen in TiO_2 with nonmetals such as N, C, and S to enhance visible-light absorption [10–13], introducing metals like La, Co, Fe, and Al into the TiO_2 lattice to narrow its bandgap [14], loading with plasmonic nanoparticles composed of metals such as Au, Ag, and Cu [6,8,15], and coupling with narrow-band-gap semiconductors to form heterojunctions [16,17]. However, lattice and doping impurity defects in TiO_2 tend to increase the recombination probability of photogenerated electron-hole pairs and decrease thermal stability, which may lower the overall quantum efficiency of TiO_2 [18,19]. Therefore, the development of visible-light-responsive TiO_2 that displays efficient photogenerated electron-hole separation

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remains of great interest [20–22].

Recently, Ti^{3+} self-doped TiO_2 showing enhanced visible-light absorption and photocatalytic performance, attributed to the introduction of a miniband below the conduction band minimum of TiO_2 , has been reported [21,23,24]. A series of synthetic approaches have been developed to prepare Ti^{3+} doped TiO_2 [25]. However, according to their electrode potentials, it is difficult to reduce Ti^{4+} to Ti^{3+} , and the reduced Ti^{3+} tends to revert to its ground state. To date, hydrogen thermal treatment [26], plasma treatment [27], ion-beam-enhanced deposition [28], vacuum activation [29], and reduction using a strong reducing agent [19] have been used to synthesize Ti^{3+} self-doped TiO_2 . Unfortunately, the multiple reaction steps, harsh reaction conditions, and complicated equipment required in these methods limit their practical application. Moreover, the post-reduction of Ti^{4+} to Ti^{3+} usually occurs on the surface of TiO_2 nanocrystals. Thus, the Ti^{3+} is easily oxidized *via* reaction with O_2 in air, resulting in poor stability.

Synthesis of nanostructured TiO_2 with well-defined pore size and high surface area has been considered another effective strategy to improve its photocatalytic performance [30]. It is expected that marked improvement of photocatalytic performance can be achieved using Ti^{3+} self-doped porous TiO_2 catalysts. However, high-temperature treatment of Ti^{3+} -doped TiO_2 catalysts may cause particle aggregation and decrease surface area, making it difficult to synthesize Ti^{3+} self-doped porous TiO_2 nanoparticles. Therefore, the development of a simple, mild strategy to synthesize Ti^{3+} -doped mesoporous TiO_2 nanocrystals with high stability is still a challenge.

Evaporation-induced self-assembly (EISA) is a versatile method that has been widely used to fabricate mesoporous metal oxides [31]. In general, EISA simply involves the preparation of a solution containing the inorganic precursor, volatile solvent, and surfactant template, followed by slow evaporation of the volatile organic solvent. In the present work, a novel economic strategy for *in situ* synthesis of Ti^{3+} self-doped mesoporous TiO_2 nanocrystals involving EISA using water as the solvent without additional reducing agent is presented. Different from the typical preparation of Ti^{3+} -doped TiO_2 by reduction, here Ti^{3+} is introduced into mesoporous TiO_2 nanocrystals through incomplete hydrolysis of TiCl_3 , forming abundant oxygen vacancies in the bulk of TiO_2 . These oxygen vacancies extend the light absorption of the photoactive TiO_2 to the visible region and effectively improve its photocatalytic performance in nitric oxide (NO) oxidation and methylene blue (MB) degradation. Unlike samples with surface Ti^{3+} doping, the Ti^{3+} self-doped mesoporous TiO_2 is stable up to 500 °C.

2. Experimental

2.1. Photocatalyst preparation

The Ti^{3+} self-doped mesoporous TiO_2 nanocrystals were fabricated by EISA. In a typical process, a precursor solution was first prepared by dissolving polyalkylene oxide block copolymer ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$, Pluronic F127, 0.54 g) as a surfactant in water (10 mL) containing 10 wt% HCl and 15 wt% TiCl_3 by

vigorous stirring for 1 h in an ice bath to form a transparent sol. The obtained sol was gelled in an open Petri dish at 40 °C in an oven for 4 d. The samples were then calcined in a muffle oven in air at 500 °C for 4 h to remove the surfactant. The obtained sample is denoted as TiO_2 -0.54-500, where 0.54 refers to the amount of surfactant and 500 refers to the calcination temperature (°C). Other samples prepared with different surfactant amounts and calcination temperatures have been labeled in a corresponding manner.

2.2. Characterization

The crystal phases of the final products were determined by X-ray diffraction (XRD, Bruker D8 Cu K_α). N_2 adsorption-desorption isotherms were recorded at –196 °C using a Micromeritics ASAP 2010 instrument. The Brunauer-Emmett-Teller (BET) specific surface area (S_{BET}), pore volume (V_{P}), and pore diameter (D_{P}) of sample were calculated by applying the BET and Barrett-Joyner-Halenda (BJH) models to desorption branches. Particle size and morphologies were observed by transmission electron microscopy (TEM; JEOL-2010F, 200 kV). Ultraviolet-visible (UV-Vis) diffuse reflectance spectra (DRS) were obtained on a Varian Cary 100 Scan UV-vis system using a barium sulfate standard as the reference. Electron paramagnetic resonance (EPR) spectra were collected on a Bruker EMX-8/2.7 EPR spectrometer at room temperature. Surface electronic state was analyzed by X-ray photoelectron spectroscopy (XPS, PerkinElmer PHI 5000).

2.3. Photocatalytic activity of Ti^{3+} self-doped mesoporous TiO_2

The photocatalytic oxidation of NO in gas phase was carried out at ambient temperature in a continuous flow reactor with volume of 18 L (420 mm × 260 mm × 166 mm) to evaluate the photocatalytic activities of different samples. During the photocatalytic oxidation process, a light source was positioned vertically above the reactor. The amount of photocatalyst used for each experiment was 0.1 g. The initial concentration of NO was about 500 ppb in an air stream (humidity level of 83%) supplied by a zero air generator. After reaching adsorption-desorption equilibrium on the photocatalyst, the light source was turned on. The concentration of NO was continuously measured by using a chemiluminescence NO analyzer (Thermo Environmental Instruments Inc., 42c). The NO removal ratio (%) was calculated using the following equation: NO removal ratio (%) = $([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}})/[\text{NO}]_{\text{in}} \times 100\%$, where $[\text{NO}]_{\text{in}}$ and $[\text{NO}]_{\text{out}}$ are the NO concentrations determined before and after photocatalytic reaction, respectively.

The photocatalytic degradation of MB was performed in aqueous solution with an initial MB concentration of 10 mg/L under the irradiation of a 300-W Xe arc lamp equipped with a UV cutoff filter (> 420 nm) positioned vertically above the suspension. A suspension of photocatalyst (50 mg) in MB solution (50 mL, 10 mg/L), was stirred for 30 min in the dark to establish adsorption-desorption equilibrium between dye and photocatalyst. At regular intervals, the catalyst was separated from the solution, and the MB concentration of the solution was an-

alyzed by a UV spectrophotometer (UV 7504/PC) at its characteristic absorption wavelength ($\lambda = 663$ nm).

3. Results and discussion

3.1. Materials characterization

The phase structure and crystallite size of the TiO_2 -0.54-500 sample were investigated by XRD, as shown in Fig. 1(a). All of the diffraction peaks could be assigned to TiO_2 , and suggested that the obtained sample was anatase phase mixed with small amount of rutile phase. The broad (101) with moderate intensity indicates that the sample is highly crystalline with a small grain size, which was calculated to be dozens of nanometers using the Scherrer formula. Fig. 1(b) reveals that the sample displayed a clear optical response in the visible region ranging from 400 to 800 nm. This is different from typical TiO_2 , which only absorbs in the UV region. Moreover, the absorption edge of the sample exhibited a considerable red shift to 422 nm compared with that of common anatase TiO_2 with an absorption edge of around 387 nm [32]. This shift is attributed to the Ti^{3+} doped in the sample originating from the incompletely reacted TiCl_3 caused by the low hydrolysis temperature used in EISA. The presence of Ti^{3+} in the sample extends the absorption of the sample to the visible region and narrows the band gap of TiO_2 by forming a miniband below the conduction band minimum of TiO_2 . The band gap energy calculated from a plot of

$(ah\nu)^{1/2}$ versus photon energy (inset of Fig. 1(b)) was 2.6 eV [5], which is much narrower than the theoretical band gap of anatase TiO_2 (3.2 eV), providing further evidence for the successful doping of the sample with Ti^{3+} .

TEM was used to further investigate the particle size and pore morphology of the sample (Fig. 1(c)). Unique worm-like particles with wider interparticle spaces were clearly observed. The particle size estimated from the TEM image was around 15 nm. Fig. 1(d) shows the N_2 adsorption-desorption isotherm and pore size distribution plots (inset) of the sample. The sample exhibited characteristic type-IV isotherm and H2-type hysteresis loops in the relative pressure (p/p_0) range of 0.6–0.8 typical of cylindrical mesopores. S_{BET} and V_p of the sample were calculated to be $71.8 \text{ m}^2/\text{g}$ and $0.129 \text{ cm}^3/\text{g}$, respectively. The average pore diameter of the sample was about 7.13 nm estimated from the desorption branch of the isotherm, with a narrow pore size distribution ranging from 2 to 15 nm. This observation is consistent with the TEM analysis. This unique Ti^{3+} self-doped mesoporous TiO_2 sample is expected to meet the requirements for high photocatalytic performance because of its narrow band gap, suitable structure to allow efficient charge separation, and large specific surface area.

To confirm the presence of Ti^{3+} embedded in the mesoporous TiO_2 sample, EPR measurements were conducted. Fig. 2(a) displays the EPR spectrum of the TiO_2 -0.54-500 sample. It has been reported that paramagnetic Ti^{3+} has a g -value of around 1.95 [19]. An intense peak centered at $g = 1.979$ was observed,

Fig. 1. Wide-angle XRD pattern (a), UV-vis absorption spectrum (b), TEM image (c), and nitrogen adsorption-desorption isotherms (d) of the TiO_2 -0.54-500 sample. The inset in (b) is a plot of $(ah\nu)^{1/2}$ against photo energy, where a represents the absorption coefficient, and that in (d) is the pore size distribution calculated using the BJH method.

demonstrating the presence of Ti^{3+} in the sample. It is well known that surface Ti^{3+} is not stable when exposed to air or water because it is easily oxidized oxygen (O_2), which is reduced to O_2^- and shows a corresponding peak around $g = 2.02$. The absence of this signal in Fig. 2(a) indicates that Ti^{3+} was mainly present in the bulk of the sample, which explains the excellent stability of our sample even under thermal treatment at 500 °C for 4 h. The surface Ti state was also investigated by XPS. As shown in Fig. 2(b), two Ti 2p binding energies located at 464.7 and 458.8 eV were attributed to Ti^{4+} . No Ti^{3+} signal was detected. It is well known that the surface Ti^{3+} is highly reactive with water and oxygen when the sample is exposed at high temperature in air, resulting in the hard detection of surface Ti^{3+} . Therefore, EPR and XPS results confirm that the Ti^{3+} was only existed in the bulk of mesoporous TiO_2 .

The calcination temperature used to prepare TiO_2 samples is of tremendous importance to achieve a mesoporous network by removing the surfactant micelles. To create porosity and initiate the crystallization of the as-prepared samples, the optimum calcination temperature and duration were investigated. Samples were prepared by changing the calcination temperature from 400 to 550 °C while maintaining the amount of surfactant F127 at 0.54 g. The changes in the degree of crystallization and phase composition of the resulting samples were revealed by XRD (Fig. 3). The textural characteristics of the calcined samples are summarized in Table 1. The crystallinity of the samples increased with calcination temperature, and no peak corresponding to the rutile phase was found for the sample calcined at 400 °C in air. A new peak located at 27.5° appeared when the calcination temperature was increased from 450 to 500 °C. This new peak can be assigned to the diffraction of the (110) plane of rutile, indicating the formation of the rutile phase. The intensity of this diffraction dramatically increased for the sample calcined at 550 °C. These observations correspond well with the reported phase transition temperature of 500 °C for the transition from anatase to thermodynamically stable rutile [33]. Meanwhile, the surface area of the sample increased with calcination temperature from 400 to 500 °C because of the efficient removal of surfactant micelles. However, a further increase of calcination temperature to 500 °C caused a decrease in surface area because of the collapse of the mesoporous structure and aggregation of TiO_2 into large

Fig. 3. Wide-angle XRD patterns of TiO_2 samples synthesized using different calcination temperatures and amounts of surfactant.

Table 1

Physicochemical properties of different Ti^{3+} self-doped TiO_2 samples.

Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
TiO_2 -0.54-400	61.0	0.128	8.41
TiO_2 -0.54-450	72.2	0.120	6.64
TiO_2 -0.54-500	71.8	0.129	7.13
TiO_2 -0.54-550	40.4	0.108	10.7
TiO_2 -0.70-500	62.0	0.154	9.93
TiO_2 -0.38-500	61.0	0.128	8.41
TiO_2 -0.22-500	52.6	0.122	9.25

nanoparticles.

To maintain the open mesopores and initiate TiO_2 crystallization, the dosage of F127 used to prepare the samples was also investigated. The mass of F127 used to synthesize Ti^{3+} self-doped TiO_2 was changed from 0.22 to 0.70 g while the calcination temperature was maintained at 500 °C. Increasing the surfactant amount slightly affected the phase composition and crystallinity of the samples, as shown in Fig. 3, but strongly affected the formation of mesopores. Using a small amount of F127 also led to a low S_{BET} . As shown in Table 1, S_{BET} initially increased from 52.6 to 71.8 m^2/g as the F127 amount was increased from 0.22 to 0.54 g. The optimum amount of surfactant F127 to maximize S_{BET} was found to be 0.54 g. Further increasing the surfactant amount above 0.54 g caused a decrease of S_{BET} .

Fig. 2. EPR spectrum (a) and Ti 2p XPS spectrum (b) of the TiO_2 -0.54-500 sample.

3.2. Photocatalytic NO oxidation

To evaluate the photocatalytic performance of the mesoporous TiO_2 samples, their photocatalytic oxidation for NO gas under simulated sunlight irradiation in a single-pass flow was investigated. Preliminary tests demonstrated that no substantial reaction of NO was observed in the absence of either light irradiation or photocatalyst, which suggests that NO was quite stable in air and the oxidation of NO was mainly driven by photocatalysis. Figure 4(a) and (b) reveal that the NO removal rate over TiO_2 -0.54-500 reached 83% and 40% under irradiation with simulated sunlight for 15 min and visible light for 30 min, respectively. The TiO_2 -0.54-500 photocatalyst showed little deactivation because only a 1% decrease in activity was observed after 1 h of photocatalytic reaction, demonstrating the excellent photocatalytic performance of the TiO_2 -0.54-500 sample under solar-light irradiation. As well known that, hydroxyl radicals and superoxide radicals, which are respectively produced by oxidation of water with photo-generated holes and reduction of oxygen with photo-generated electrons, play a vital role in photocatalytic oxidation of NO [5,8]. In this case, the formation processes of hydroxyl radicals and superoxide radicals were facilitated by introducing Ti^{3+} into the framework of mesoporous TiO_2 to enhance the visible light absorption. Moreover, the mesoporous structure has great advantage of a rapid photo-charge and mass transfer. As shown in Fig. 5, the recovered TiO_2 -0.54-500 sample displayed excellent durability and could be continuously used for 3.5 h without marked loss

in activity, further suggesting the high stability of the Ti^{3+} self-doped sample.

As illustrated in Fig. 4(a) and (c), the calcination temperature and surfactant amount only slightly affected the photocatalytic performance of the samples toward NO oxidation under simulated solar irradiation because of the presence of 2%–5% UV light. Therefore, all samples were effectively activated under simulated solar light. However, the TiO_2 -0.54-400, TiO_2 -0.54-450, and TiO_2 -0.54-550 samples displayed poor NO oxidation reactivity under visible-light irradiation. This could be attributed to the following reasons: (1) a low calcination temperature resulted in low crystallinity and inefficient removal of the surfactant; (2) a high calcination temperature caused a decrease in specific surface area and increase of TiO_2 particle size (Fig. 3 and Table 1); (3) a high calcination temperature promoted oxidation of Ti^{3+} , leading to a decrease in the concentration of Ti^{3+} doped in mesoporous TiO_2 ; (4) inefficient absorption of visible light because of the loss of Ti^{3+} at high temperature. Therefore, the photocatalytic activity of TiO_2 -0.54-550 was much lower than that of TiO_2 -0.54-500. In contrast, the dosage of F127 used to synthesize mesoporous TiO_2 has only a slight influence on photocatalytic activity under visible-light irradiation. The optimum surfactant amount for the photocatalytic oxidation of NO was found to be 0.54 g, which might be because the dosage of surfactant only affected the mesoporous structure and surface area of the samples. Based on the above photocatalytic performance, we can conclude that the presence of Ti^{3+} played important roles in ex-

Fig. 4. Influence of calcination temperature (a, b) and surfactant amount (c, d) on the photocatalytic oxidation of NO under irradiation with either simulated sunlight (2×150 -W halogen lamps) or visible light (2×150 -W halogen lamps equipped with a UV cutoff filter (>420 nm)).

Fig. 5. Stability of recovered $\text{TiO}_2\text{-0.54-500}$ in photocatalytic oxidation of NO. The photocatalyst was washed thoroughly with water after 1 h of photocatalytic reaction and dried under vacuum at 80°C before reuse.

tending the light absorption of the samples to the visible region and narrowing the band gap of TiO_2 by forming a miniband below the conduction band minimum of TiO_2 .

3.3. Photocatalytic degradation of MB

To further investigate the photocatalytic performance of the samples, the degradation of MB in aqueous solution under visible-light irradiation was measured as another photoreaction probe. As shown in the Fig. 6, no significant degradation of MB was observed in the absence of catalyst under visible light irradiation. After 30 min dark reaction, about 6% of MB was adsorbed on catalysts, which was due to the large surface area of catalysts. Figure 6 reveals that the concentration of MB decreased continuously with increasing irradiation time in the presence of $\text{TiO}_2\text{-0.54-500}$. Almost 100% of MB was photocatalytically degraded after 2 h, so $\text{TiO}_2\text{-0.54-500}$ displayed excellent visible-light-driven photocatalytic activity. The MB solution changed from dark blue to colorless during this time (lower left inset of Fig. 6), visually demonstrating the high photocatalytic activity of $\text{TiO}_2\text{-0.54-500}$. These results show that the photocatalytic degradation efficiency of TiO_2 under visible-light irradiation can be markedly enhanced by introducing Ti^{3+} into the framework of mesoporous TiO_2 . Therefore, the synergistic effect between Ti^{3+} and mesoporous structure of TiO_2 on narrowing the band gap of TiO_2 , enhancing visible light harvesting, and promoting photo-excited charge separation can actually be applied to improve photocatalytic activity [34].

4. Conclusions

We developed a new approach for *in situ* synthesis of Ti^{3+} self-doped mesoporous TiO_2 via a simple one-step EISA method without additional reductant and subsequent calcination. The mesoporous structure and self-doped Ti^{3+} of the sample are responsible for its enhanced light absorption and photocatalytic activity toward the oxidation of gas-phase NO and photocatalytic degradation of MB in the liquid phase under light irradiation. The present work demonstrates a simple, mild, and economical method to narrow the band gap of TiO_2 through

Fig. 6. Degradation of MB in the presence of $\text{TiO}_2\text{-0.54-500}$. The lower left and upper right insets are photographs and UV-vis spectra of the MB solutions after different reaction time, respectively.

one-step Ti^{3+} self-doping, allowing the development of a highly active and stable photocatalyst that may solve various global environmental problems.

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Graphical Abstract

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In situ synthesis of Ti^{3+} self-doped mesoporous TiO_2 as a durable photocatalyst for environmental remediation

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A facile approach for *in situ* synthesis of titanium(III) self-doped mesoporous TiO_2 is developed. The product exhibits high photocatalytic activity and stability in the oxidation of nitric oxide in air and photochemical degradation of methylene blue.

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原位合成稳定的 Ti^{3+} 自修饰介孔 TiO_2 光催化剂在环境净化中的应用

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摘要: 半导体光催化剂 TiO_2 因具有绿色环保无污染、化学稳定性好及可实现稳定产氢等优点而广泛应用于光解水、废水处理和空气净化等领域。然而, 锐钛矿相 TiO_2 禁带宽度约为3.2 eV, 仅对紫外光响应。而在太阳光中, 44%左右为可见光, 紫外光仅占不到4%。为了提高 TiO_2 对太阳光的利用率和在可见光照射下的光催化活性, 近年来人们采用掺杂金属/非金属离子以及可见光催化剂复合等方法对 TiO_2 进行改性。但是这些离子掺杂的方法会不可避免地在 TiO_2 晶格中形成结构缺陷, 这些结构缺陷作为光生电子和空穴的复合中心不利于电子和空穴分离。最近研究表明, 通过 Ti^{3+} 自掺杂可以很好提高 TiO_2 可见光催化活性, 但是目前制备 Ti^{3+} 掺杂 TiO_2 的方法较复杂, 形成的 Ti^{3+} 掺杂易在表面积聚而被进一步氧化, 影响其光催化稳定性, 不利于实际应用。因此, 开发具有良好电子-空穴分离效率的可见光催化剂引起了广泛的研究兴趣。

本文通过原位自掺杂 Ti^{3+} 来提高 TiO_2 可见光光催化活性。以 TiCl_3 为钛源, H_2O 为溶剂, F127为软模板, 采用溶剂挥发诱导自组装的方法制备了蠕虫状 Ti^{3+} 自掺杂的介孔 TiO_2 。采用X射线衍射(XRD)、 N_2 物理吸附、紫外-可见漫反射(UV-vis)、透射电子显微镜和电子顺磁共振(EPR)对所制备样品结构、结晶度和形貌等进行了表征分析。通过控制表面活性剂用量和焙烧温度优化了 Ti^{3+} 自掺杂介孔 TiO_2 的光催化活性。结果表明, 在模拟太阳光照射下, 所制样品对气相光催化氧化NO和水相降解有机染料亚甲基蓝表现出优异的催化性能和稳定性。 Ti^{3+} 自掺杂介孔 TiO_2 有效扩展了催化剂的光吸收范围, 提高了光生电子空穴的迁移效率。其优异的光催化活性和稳定性主要归因于掺杂在 TiO_2 骨架中的 Ti^{3+} 和所合成催化剂多孔性之间的协同效果。

固体UV-vis结果表明, 所合成的 TiO_2 具有很好的可见光响应, 主要归因于在 TiO_2 材料合成过程中, 部分 Ti^{3+} 未被完全氧化, Ti^{3+} 掺入可以有效降低 TiO_2 的禁带宽度。通过计算可知合成的 TiO_2 禁带宽度为2.7 eV。通过低温EPR测试进一步证明了 Ti^{3+} 的存在, 而且 Ti^{3+} 主要掺杂在 TiO_2 体相中。 N_2 物理吸附结果表明, 随焙烧温度不断提高, 所得产物的比表面积先增加后减少, 当焙烧温度在

500 °C时, 比表面积最大, 但至550 °C时, 比表面积、孔径和孔体积增大, 表明催化剂的孔结构被破坏. 表面活性剂F127的用量对样品比表面积和孔径大小也有影响, 当其用量为0.54 g时, 所得产物的比表面积最大.

我们将所合成的TiO₂应用于污染气体NO的氧化, 考察了焙烧温度和表面活性剂用量对光催化剂性能的影响. 结果表明, 当表面活性剂用量为0.54 g, 焙烧温度为500 °C时, 所制催化剂在模拟太阳光和可见光照射下都表现出最好的NO去除转化率. 将使用过的催化剂离心洗涤后进行连续反应3.5 h, 依然保持很高的NO去除转化率. 催化剂高活性及稳定性的主要原因是Ti³⁺的掺杂将TiO₂光响应范围拓展到可见光区域, 且Ti³⁺掺杂和介孔结构之间的协同作用有利于促进光生电子和空穴的分离. 当催化剂在低于500 °C焙烧时, 所得催化剂结晶度较低, 不利于光生电子-空穴的分离, 而高温焙烧则会导致催化剂介孔结构遭到破坏, 不利于NO气体吸附和产物脱附. 表面活性剂对催化剂活性影响较小, 在可见光照射下催化剂均表现出很好的光催化活性. 此外, 该Ti³⁺自掺杂介孔TiO₂在液相条件下对有机染料亚甲基蓝也表现出很好的去除效果, 可见光照射2 h, 亚甲基蓝去除率接近100%.

关键词: 钛(III)自掺杂; 介孔二氧化钛; 溶剂挥发诱导自组装; 一氧化氮氧化; 光催化

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