

Preparation of High Activity $\text{TiO}_2/\text{g-C}_3\text{N}_4$ Photocatalysts via a Facile Sol-gel Method with $\text{Ti}(\text{OBU})_4$ as Ti Source and Melamine as Nitrogen Source

Zhang Chunyong¹, Li Mingshi², Lu Mohong², Zhang Guohua¹, Zheng Chunzhi¹,
Wen Yingpin¹, Cheng Jiehong¹

¹ Jiangsu Key Laboratory of Precious Metal Chemistry and Technology, Jiangsu University of Technology, Changzhou 213001; ² Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, China

Abstract: A highly active photocatalyst $\text{TiO}_2/\text{g-C}_3\text{N}_4$ was synthesized by a facile two-step method including sol-gel and calcination, using $\text{Ti}(\text{OBU})_4$ as a Ti source and melamine as a nitrogen source. The resultant photocatalysts were characterized by XRD, TEM and UV-vis diffuse reflectance spectra. The results show that $\text{TiO}_2/\text{g-C}_3\text{N}_4$ is formed and TiO_2 is beset with graphite-like carbon nitride of layer structure. $\text{TiO}_2/\text{g-C}_3\text{N}_4$ exhibits obviously enhanced visible light photocatalytic activity, and the degradation efficiency of Methylene blue (MB) reaches 94.46% after irradiation for 1 h, which is much higher than that of $\text{g-C}_3\text{N}_4$ and TiO_2 . The improved photocatalytic activity of $\text{TiO}_2/\text{g-C}_3\text{N}_4$ is attributable to its wide spectrum responsive range, strong visible light adsorption capability, and the synergistic effect between TiO_2 and $\text{g-C}_3\text{N}_4$. The mechanism of photocatalytic reaction was discussed.

Key words: photocatalyst; TiO_2 ; $\text{g-C}_3\text{N}_4$; visible light photocatalytic activity

Semiconductor photocatalysis has attracted much attention in the past few decades because of its extensive applications in the fields of renewable hydrogen energy supply and environmental protection^[1]. TiO_2 is the most promising photoelectrode semiconductor material owing to its nontoxicity, low cost, and cyclic stability^[2]. However, owing to the large band gap energy of anatase TiO_2 , UV light is vital to its photocatalytic reaction^[3]. As a result, tremendous efforts such as doping, deposition of metals and hybrid composite have been employed to enhance visible light photocatalytic activity of TiO_2 ^[2,3].

As a novel function material, $\text{g-C}_3\text{N}_4$ has attracted much attention in recent years for its particular properties, high electron mobility and metal-free with visible light absorption^[4]. $\text{g-C}_3\text{N}_4$ has superior reduction ability due to the low band gap^[4]. However, its oxidation ability is inferior as compared to TiO_2 ^[5]. Currently, a number of

synthesis routes of hybrid $\text{TiO}_2/\text{g-C}_3\text{N}_4$ have been introduced by treatment of the mixture of TiO_2 and C_3N_4 ^[6-8], TiO_2 and nitrogen source^[9] or the mixture of Ti source and C_3N_4 ^[10-14] to overcome these drawbacks.

To the best of our knowledge, the preparation of $\text{TiO}_2/\text{g-C}_3\text{N}_4$ from the Ti source and the nitrogen source has not been reported. Therefore, $\text{TiO}_2/\text{g-C}_3\text{N}_4$ was synthesized by a two-step method of sol-gel and calcination using $\text{Ti}(\text{OBU})_4$ as the Ti source and melamine as the nitrogen source to improve photocatalytic activity under visible light irradiation in the present paper.

1 Experiment

The $\text{TiO}_2/\text{g-C}_3\text{N}_4$ photocatalysts were facilely synthesized by a two-step method of sol-gel and calcination. The detailed synthesis procedure was as follows. 30 mL of $\text{Ti}(\text{OBU})_4$ and 20 g of melamine were combined in 500 mL

Received date: February 14, 2016

Foundation item: National Natural Science Foundation of China (21307009); University Science Research Project of Jiangsu Province (13KJB530004)

Corresponding author: Lu Mohong, Ph. D., Associate Professor, Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, P. R. China, Tel: 0086-519-86330360, E-mail: mlu@cczu.edu.cn

Copyright © 2017, Northwest Institute for Nonferrous Metal Research. Published by Elsevier BV. All rights reserved.

of ethanol to obtain a mixture solution which was vigorously stirred at room temperature for 30 min. Deionized water (40 mL) was added into the above mixture while stirring, and the sol-gel was obtained. The sol-gel was placed in a drying oven at 80 °C under vacuum for 24 h to give a light yellow precipitate of precursor of TiO₂/g-C₃N₄. The precursor was then annealed in a covered muffle furnace at 520 °C for 2 h with a heating rate of 2 °C/min to yield the TiO₂/g-C₃N₄ photocatalyst. For comparison, pure TiO₂ and g-C₃N₄ were synthesized using a similar procedure for preparing TiO₂/g-C₃N₄ in the absence of melamine and Ti(OBu)₄, respectively.

The crystal structures of the samples were characterized by X-ray diffraction (XRD) measurement (D/MAX-2500PC). The morphologies of the samples were obtained on a JEOL 2010 high-resolution transmission electron microscopy (TEM). Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) spectra of the photocatalysts were measured by a UV-vis scanning spectrophotometer (Shimadzu UV-2700).

The photocatalytic activities of all prepared photocatalysts were investigated under visible light irradiation from 300 W Xe lamp (Philips, China) with a 400 nm cutoff filter to eliminate the UV light. 20 mg of catalyst was added to 20 mL of aqueous solution of Methylene blue (MB) dye (20 mg/L). In order to ensure that the photocatalyst was well dispersed in the MB solution, prior to irradiation, the suspension was initially treated with ultrasonic stirring for 10 min, followed by magnetically stirring in the dark for 30 min to establish an adsorption-desorption equilibrium. Once the concentration of MB has stabilized, the sample was exposed to the Xe light irradiation. At given time intervals, 2~3 mL of sample suspension was withdrawn and centrifuged at 12 000 r/min for 10 min to remove the photocatalyst. The clarified solution was analyzed by UV759 UV-vis spectrometer (Shanghai Precision & Scientific Instrument Co., Ltd, China) to obtain the absorbance of MB at the maximum absorption wavelength of 664 nm. The concentration of MB was calculated by a calibration curve. The degradation efficiency (*D*) of MB could be calculated by $D=(1-C_t/C_0)\times 100\%$, where *C*₀ and *C*_{*t*} are the equilibrium concentration of MB before and after visible light irradiation, respectively.

2 Results and Discussion

2.1 XRD analysis

The XRD patterns of TiO₂, TiO₂/g-C₃N₄ and g-C₃N₄ are shown in Fig.1. It is obvious that the as-synthesized TiO₂ can be indexed to the anatase TiO₂, which is in agreement with standard data (JCPDS file No.21-1272). It can be seen that the pure g-C₃N₄ shows two characteristic diffraction peaks around 13.32° and 27.29° as a result of graphite, relating to the characteristic interlayer stacking structure

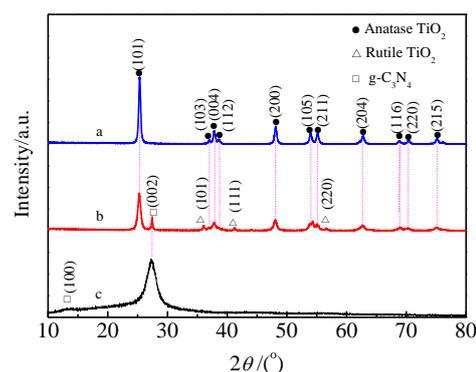


Fig.1 XRD patterns of TiO₂ (a), TiO₂/g-C₃N₄ (b), and g-C₃N₄ (c)

(JCPDS 87-1526)^[4]. In addition, the XRD pattern of TiO₂/g-C₃N₄ reveals its crystalline phase, which is a mixture of g-C₃N₄, anatase and rutile crystals. This implies that anatase TiO₂ can be partly converted into anatase TiO₂ under the annealing condition. The absence of a small characteristic peak of g-C₃N₄ at 13.32° is attributed to the relatively low diffraction intensity of g-C₃N₄^[15]. The *d* value for (002) plane of g-C₃N₄ and TiO₂/g-C₃N₄ is 0.326 nm and 0.325 nm, respectively. The difference of *d* value for (002) between g-C₃N₄ and TiO₂/g-C₃N₄ is hardly recognized. Therefore, this suggests that the structural change of g-C₃N₄ in TiO₂/g-C₃N₄ does not occur. The characteristic diffraction peaks of TiO₂ and g-C₃N₄ can be found in the XRD pattern of TiO₂/g-C₃N₄, indicating the hybridization of TiO₂ with g-C₃N₄^[16].

2.2 TEM analysis

Fig.2 show the morphologies of TiO₂, g-C₃N₄ and TiO₂/g-C₃N₄. The results are in good agreement with the XRD data. The graphite-like g-C₃N₄ (Fig.2b) has thin amorphous sheets with an irregular shape, which is consistent with the typical morphology of g-C₃N₄. The amorphous layer is attributed to the carbon nitride polymeric layered structure as supported by the XRD pattern (Fig.1c). TiO₂ (Fig.2a) shows a certain degree of particle agglomeration with an irregular shape and the size is in the range of 20~40 nm. The TEM images of TiO₂/g-C₃N₄ (Fig.2c) show that spherical TiO₂ particles are evenly dispersed on thin g-C₃N₄ layers.

2.3 UV-vis diffuse reflectance spectra

Fig.3 shows the UV-vis DRS of TiO₂, g-C₃N₄ and TiO₂/g-C₃N₄. From the figure, it is obvious that TiO₂ mostly absorbs UV light with a little visible light. g-C₃N₄ absorbs light with wavelength up to 394 nm, where its absorption in UV is lower than that of TiO₂. The absorption edges of TiO₂/g-C₃N₄ shift remarkably to the visible light region from 390 to 550 nm as compared to TiO₂ and g-C₃N₄, indicating that the photo response of the TiO₂/g-C₃N₄ extends to the visible light region due to the combination of TiO₂ and g-C₃N₄. Therefore, TiO₂/g-C₃N₄ can absorb large

amounts of visible light, and it may be a suitable visible irradiation photocatalyst.

2.4 Photocatalytic activity

The photocatalytic activities of all prepared photocatalysts under visible light irradiation by the degradation of MB in aqueous solution are shown in Fig.4. In addition to experiments with the photocatalyst and irradiation, the blank experiment under visible-light irradiation without the photocatalyst was also investigated. The blank experiment shows that the self-degradation of MB is slow and the degradation efficiency is less than 10.04% after visible light irradiation for 60 min, which demonstrates the photocatalytic activity of the photocatalyst in the process of MB decomposition. While the degradation efficiency for TiO₂, g-C₃N₄ and TiO₂/g-C₃N₄ is approximately 81.81%, 45.21% and 94.46%, respectively. The TiO₂/g-C₃N₄ is exposed to visible light irradiation and shows much higher catalytic capability towards degrading dye MB compared with TiO₂

and g-C₃N₄, indicating that TiO₂/g-C₃N₄ possesses remarkable photocatalytic activity under visible light.

2.5 Proposed photocatalytic mechanism

Although g-C₃N₄ has lower band gap than TiO₂/g-C₃N₄ and TiO₂, its photocatalytic activities are far inferior to those of TiO₂/g-C₃N₄ and TiO₂ due to the low intensity of the absorption spectra of g-C₃N₄ (Fig.3). The TiO₂/g-C₃N₄ has a high photocatalytic activity and its photocatalytic efficiency is higher than those of the pure TiO₂ or g-C₃N₄ alone although its band-gap energy is between the pure TiO₂ and g-C₃N₄. Therefore, the effects of intensity, wavelength and the combination are important.

On the basis of the above results, the superior photocatalytic activity of TiO₂/g-C₃N₄ under visible light can be firstly explained in terms of its wide spectrum responsive range and strong visible light adsorption capability. This means there are more photons absorbed by the catalysts in the visible region and more photo-generated electrons participating in the MB degradation process.

Referring to previous literature^[3,5], the enhanced photocatalytic activity of TiO₂/g-C₃N₄ may be mainly attributed to its synergistic effect between TiO₂ and g-C₃N₄, which

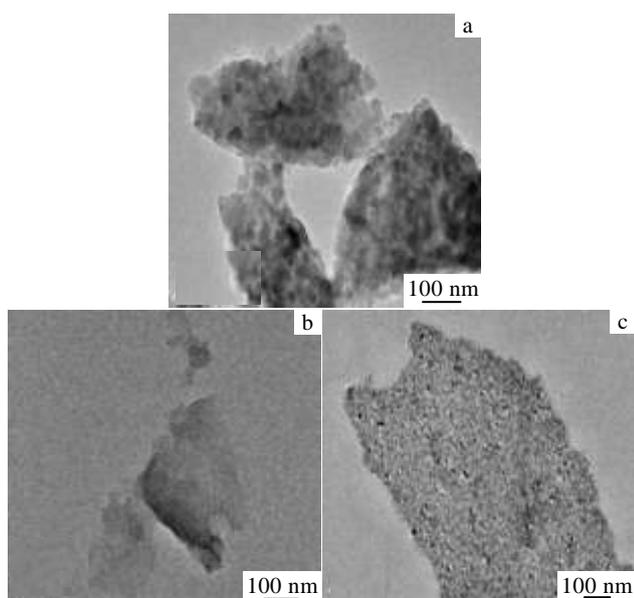


Fig.2 TEM images of TiO₂ (a), g-C₃N₄ (b), and TiO₂/g-C₃N₄ (c)

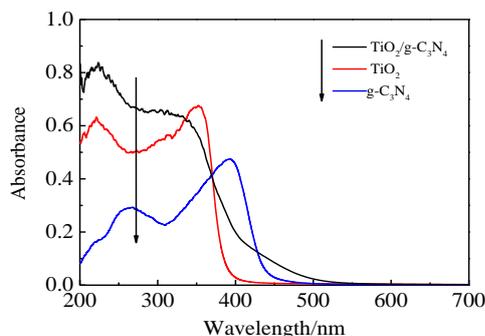


Fig.3 UV-vis DRS spectra of TiO₂, g-C₃N₄ and TiO₂/g-C₃N₄

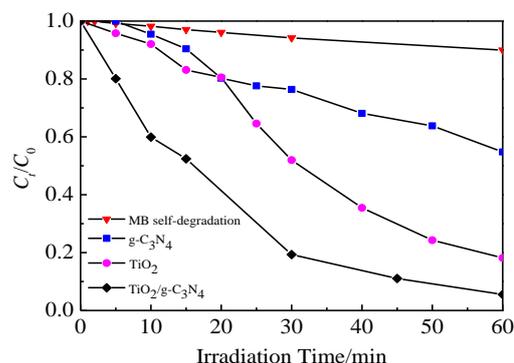


Fig.4 Photocatalytic activities of TiO₂, TiO₂/g-C₃N₄ and g-C₃N₄ under visible light irradiation

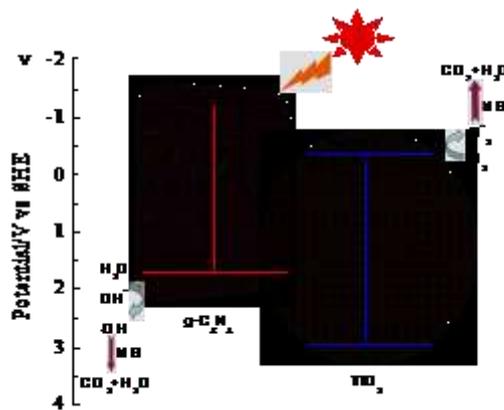


Fig.5 Schematic illustration of the photocatalytic mechanism of the TiO₂/g-C₃N₄

promotes the effective separation of the photogenerated electron-hole pairs and thus allows fast charge transfer, charge separation and stabilization^[6]. The photocatalytic mechanism is shown in Fig.5. Because of the low band gap energy (2.92 eV), g-C₃N₄ can easily absorb the photons under visible light irradiation to generate plenty of electrons and holes in its conduction and valence band, respectively. The holes on the g-C₃N₄ surface are rapidly scavenged by H₂O and OH⁻, generating ·OH to oxidize MB. The electrons in the conduction band of g-C₃N₄ are easy to transfer through the smooth heterojunction interface between TiO₂ and g-C₃N₄ to the conduction band of TiO₂ particles because the conduction band of TiO₂ (-0.335 eV) is lower than that of g-C₃N₄ (-1.600 eV), which effectively restrains the recombination process of the electron-hole pairs. The electrons on the conduction band of TiO₂ can be captured by electrophilic O₂, generating O₂⁻^[17,18]. And then O₂⁻ oxidizes MB to produce CO₂ and H₂O and enhances the photocatalytic activity of TiO₂/g-C₃N₄ composite for degradation of MB.

3 Conclusions

1) The efficient photocatalytic TiO₂/g-C₃N₄ photocatalysts are synthesized by a simple method of sol-gel and calcination.

2) Dispersed TiO₂ is supported on g-C₃N₄ particles. The enhanced visible light photocatalytic activity of TiO₂/g-C₃N₄, which is higher than that of TiO₂ and g-C₃N₄, is probably ascribed to its wide spectrum responsive range, strong adsorption capability, and the synergistic effect between TiO₂ and g-C₃N₄. It effectively enhances separation of photogenerated electron-hole pairs during the photocatalytic process.

References

- Hoffmann M R, Martin S T, Choi W et al. *Chemical Reviews*[J], 1995, 95(1): 69
- Liu G, Yu J C, Lu G Q et al. *Chemical Communications*[J], 2011, 47(24): 6763
- Chen X, Liu L, Yu P Y et al. *Science*[J], 2011, 331(6018): 746
- Wang X, Blechert S, Antonietti M. *ACS Catalysis*[J], 2012, 2(8): 1596
- Kondo K, Murakami N, Ye C et al. *Applied Catalysis B: Environmental*[J], 2013, 142-143: 362
- Yan H J, Yang H X. *J Alloy Compd*[J], 2011, 509(4): L26
- Miranda C, Mansilla H, Yáñez J et al. *Journal of Photochemistry and Photobiology A: Chemistry*[J], 2013, 253: 16
- Gu L A, Wang J Y, Cheng H et al. *ACS Applied Materials & Interfaces*[J], 2013, 5(8): 3085
- Wang J X, Huang J, Xie H L et al. *International Journal of Hydrogen Energy*[J], 2014, 39(12): 6354
- Yang N, Li G Q, Wang W L et al. *Journal of Physics and Chemistry of Solids*[J], 2011, 72(11): 1319
- Dai K, Lu L H, Liang C H et al. *Applied Catalysis B: Environmental*[J], 2014, 156-157: 331
- Gu L A, Wang J Y, Zou Z J et al. *Journal of Hazardous Materials*[J], 2014, 268: 216
- Boonprakob N, Wetchakun N, Phanichphant S et al. *Journal of Colloid and Interface Science*[J], 2014, 417: 402
- Zhang L, Jing D W, She X L et al. *Journal of Materials Chemistry A*[J], 2014, 2(7): 2071
- Zhao S S, Chen S, Yu H T et al. *Separation and Purification Technology*[J], 2012, 99: 50
- Chen X F, Wei J, Hou R J et al. *Applied Catalysis B: Environmental*[J], 2016, 188: 342
- Liang Y H, Wang H, Liu L et al. *Rare Metal Materials and Engineering*[J], 2015, 44(5): 1088
- Zhang Y J, Kang L, Liu L C. *Rare Metal Materials and Engineering*[J], 2015, 44(12): 3032 (in Chinese)

以 Ti(OBu)₄ 为钛源、三聚氰胺为氮源通过溶胶-凝胶法制备高活性光催化剂 TiO₂/g-C₃N₄

- 张春勇¹, 李明时², 鲁墨弘², 张国华¹, 郑纯智¹, 文颖频¹, 程洁红¹
 (1. 江苏理工学院 江苏省贵金属深加工技术及应用重点建设实验室, 江苏 常州 213001)
 (2. 常州大学 江苏省精细石油化工重点实验室, 江苏 常州 213164)

摘要: 以 Ti(OBu)₄ 为钛源、三聚氰胺为氮源, 通过溶胶-凝胶和高温煅烧两步法制备了高活性可见光光催化剂 TiO₂/g-C₃N₄。利用 X 射线衍射 (XRD)、透射电子显微镜 (TEM) 和紫外-可见漫反射光谱 (UV-vis diffuse reflectance spectra) 等手段对其进行了表征。结果表明: TiO₂ 镶嵌在石墨相的 g-C₃N₄ 中, 并与 g-C₃N₄ 构成 TiO₂/g-C₃N₄ 复合材料。由于 TiO₂ 与 g-C₃N₄ 的协同作用, 扩大了 TiO₂/g-C₃N₄ 的可见光吸收范围和强度, 因而具有很好的可见光光催化性能。

关键词: 光催化剂; TiO₂; g-C₃N₄; 可见光光催化

作者简介: 张春勇, 男, 1978 年生, 硕士, 副教授, 江苏理工学院化学与环境工程学院, 江苏 常州 213001, 电话: 0519-86989073, E-mail: zhangcy@jsut.edu.cn