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Synthesis of $\text{TiO}_2/\text{g-C}_3\text{N}_4$ nanocomposites with phosphate–oxygen functional bridges for improved photocatalytic activity

Chong Liu ^{a,b}, Fazal Raziq ^a, Zhijun Li ^a, Yang Qu ^a, Amir Zada ^a, Liqiang Jing ^{a,*}^a Key Laboratory of Functional Inorganic Materials Chemistry, Heilongjiang University, Harbin 150080, Heilongjiang, China^b College of Environmental and Chemical Engineering, Heilongjiang University of Science and Technology, Harbin 150027, Heilongjiang, China

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ABSTRACT

One of the most general methods to enhance the separation of photogenerated carriers for $\text{g-C}_3\text{N}_4$ is to construct a suitable heterojunctional composite, according to the principle of matching energy levels. The interface contact in the fabricated nanocomposite greatly influences the charge transfer and separation so as to determine the final photocatalytic activities. However, the role of interface contact is often neglected, and is rarely reported to date. Hence, it is possible to further enhance the photocatalytic activity of $\text{g-C}_3\text{N}_4$ -based nanocomposite by improving the interfacial connection. Herein, phosphate–oxygen (P–O) bridged $\text{TiO}_2/\text{g-C}_3\text{N}_4$ nanocomposites were successfully synthesized using a simple wet chemical method, and the effects of the P–O functional bridges on the photogenerated charge separation and photocatalytic activity for pollutant degradation and CO_2 reduction were investigated. The photocatalytic activity of $\text{g-C}_3\text{N}_4$ was greatly improved upon coupling with an appropriate amount of nanocrystalline TiO_2 , especially with P–O bridged TiO_2 . Atmosphere-controlled steady-state surface photovoltage spectroscopy and photoluminescence spectroscopy analyses revealed clearly the enhancement of photogenerated charge separation of $\text{g-C}_3\text{N}_4$ upon coupling with the P–O bridged TiO_2 , resulting from the built P–O bridges between TiO_2 and $\text{g-C}_3\text{N}_4$ so as to promote effective transfer of excited electrons from $\text{g-C}_3\text{N}_4$ to TiO_2 . This enhancement was responsible for the improved photoactivity of the P–O bridged $\text{TiO}_2/\text{g-C}_3\text{N}_4$ nanocomposite, which exhibited three-time photocatalytic activity enhancement for 2,4-dichlorophenol degradation and CO_2 reduction compared with bare $\text{g-C}_3\text{N}_4$. Furthermore, radical-trapping experiments revealed that the $\cdot\text{OH}$ species formed as hole-modulated direct intermediates dominated the photocatalytic degradation of 2,4-dichlorophenol. This work provides a feasible strategy for the design and synthesis of high-performance $\text{g-C}_3\text{N}_4$ -based nanocomposite photocatalysts for pollutant degradation and CO_2 reduction.

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1. Introduction

Environmental pollution, the greenhouse effect, and resource shortages have become serious social problems. As an

effective green technology, semiconductor photocatalysis shows great potential for solving these energy and environmental issues. An ideal semiconductor photocatalyst should exhibit a reasonable band structure, excellent light-absorption

* Corresponding author. Tel/Fax: +86-451-86604760; E-mail: jinglq@hlju.edu.cn

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properties, improved photogenerated charge separation, non-toxicity, and no secondary pollution. Unfortunately, a single traditional semiconductor photocatalyst cannot fulfill all of these requirements. Therefore, novel semiconductor photocatalysts and their composites are being widely studied.

Graphitic carbon nitride (g-C₃N₄) is a metal-free polymeric photocatalyst that has received considerable attention because of its suitable energy band gap (2.7 eV), high stability, and unique surface properties [1]. Moreover, because of its appropriate valence (1.4 eV) and conduction band (−1.3 eV) positions, g-C₃N₄ is regarded as a promising photocatalyst in the field of sustainable energy for CO₂ conversion, water splitting, and pollutant degradation [2–4]. However, its relatively narrow visible-light response, small surface area, and rather high photogenerated charge recombination greatly affect its photocatalytic performance, limiting its wide practical application. Several attempts have been made to overcome these shortfalls, mainly by tuning its microstructure, with certain successes [5–8].

One of the most effective methods to improve the photocatalytic activity of g-C₃N₄ is to construct heterogeneous composites with suitable bandgap semiconductors by matching their energy levels. Thus far, several wide-bandgap oxides (such as TiO₂, ZnO, and SnO₂) have been coupled with g-C₃N₄ to efficiently improve its photocatalytic activity [9–15]. It is generally accepted that the photogenerated electrons transfer from the conduction band of g-C₃N₄ to that of the coupled oxide to prolong the lifetime and enhance the separation of photogenerated charges, thereby improving the photocatalytic activity.

The interfacial connection of heterogeneous semiconductors is also expected to greatly affect the charge transfer and separation in the fabricated composite. However, previous studies mainly focused on various compounds, synthetic methods, and morphologies [16–20], while the effective connections between the interfaces often being neglected. It is widely accepted that the connection of different parts in a nanocomposite mainly depends on the degree of lattice matching. TiO₂ and g-C₃N₄ possess different crystal structures with different lattice parameters, indicating that their connections are weak. Hence, further enhancement of the photocatalytic activity of TiO₂/g-C₃N₄ nanocomposites is possible by improving their interfacial connection. However, to date, no phosphate–oxygen (P–O) bridges have been built in TiO₂/g-C₃N₄ nanocomposites, according to the relevant literature. Our previous works indicate that the introduction of P–O and silicate–oxygen (Si–O) functional bridges is beneficial for the charge transfer and separation in TiO₂/Fe₂O₃ and ZnO/BiVO₄ nanocomposites, respectively [21,22]. Thus, improvement of the photocatalytic performance of g-C₃N₄-based heterojunction nanocomposites by building P–O functional bridges is feasible.

In this work, the effects of P–O functional bridges on the photogenerated charge transfer and separation of TiO₂/g-C₃N₄ nanocomposites were investigated. The introduction of P–O functional bridges resulted in positive effects, leading to improved photocatalytic activity. Notably, the P–O bridged TiO₂/g-C₃N₄ nanocomposite exhibited a three-time enhancement in photoactivity for the degradation of 2,4-dichlorophenol

(2,4-DCP) and CO₂ reduction. This work will provide feasible routes for the synthesis of g-C₃N₄-based nanophotocatalysts for efficient photocatalysis.

2. Experimental

All the chemicals used in this work were of analytical grade and used without further purification.

2.1. Fabrication of P–O bridged TiO₂/g-C₃N₄ nanocomposites

g-C₃N₄ was synthesized by heating dicyandiamide in a ceramic crucible at 550 °C for 4 h (5 °C/min) [23].

To prepare the TiO₂/g-C₃N₄ nanocomposites, 2 g of the prepared g-C₃N₄ was impregnated in a mixed solution of 5 mL of distilled water, 1 mL of HNO₃, and 20 mL of ethanol, and then, 6 mL of ethanol solution of tetrabutyl titanate (volume ratio of 9:1) was added dropwise with continuous stirring for 2 h. The suspension was subsequently dried at 70 °C, followed by thermal treatment at 450 °C for 1 h.

To introduce P–O bridges into the TiO₂/g-C₃N₄ nanocomposites, phosphate-capped TiO₂ was synthesized in advance by mixing TiO₂ powder (which was synthesized using the method previously described without g-C₃N₄) with various amounts of 0.5 mmol/L phosphoric acid solution with vigorous stirring for 2 h. Then, the suspension was dried and calcined at 450 °C for 1 h. Next, g-C₃N₄ was coupled with the phosphate-capped TiO₂ using the synthetic procedure for TiO₂/g-C₃N₄. The TiO₂/g-C₃N₄ and P–O bridged TiO₂/g-C₃N₄ nanocomposite samples were defined as T/CN and T-XPB-CN, respectively, where *X* indicates the molar percent ratio of phosphate to TiO₂, and T, PB, and CN represent TiO₂, P–O bridges, and g-C₃N₄, respectively.

2.2. Characterization

The crystalline phases of the as-prepared samples were characterized using X-ray diffraction (XRD; Bruker D8) with a Cu K_α radiation source ($\lambda = 0.15418$ nm); an accelerating voltage of 30 kV and emission current of 20 mA were employed. The morphologies of the samples were examined using transmission electron microscopy (TEM; JEOL JEM-2010) at an operating voltage of 200 kV. Light absorption of the samples was analyzed using Ultraviolet-visible (UV-vis) diffuse reflectance spectroscopy (Shimadzu UV-2550). Fourier-transform infrared (FTIR) spectroscopy was performed to certify the surface composition using a spectrometer (Bruker Equinox 55) with KBr used for dilution.

To investigate the actions of photogenerated charges, steady-state surface photovoltage spectroscopy (SS-SPS) and Photoluminescence (PL) spectroscopy measurements were performed. The SS-SPS measurements of the samples were conducted using a lab-made apparatus with a lock-in amplifier (SR830) synchronized with a light chopper (SR540). The powder sample was sandwiched between two indium tin oxide glass electrodes, and the outer electric field was employed. The sandwiched electrodes were arranged in an atmosphere-controlled container with a quartz window, and mono-

Fig. 1. XRD patterns (a) and DRS spectra (b) of T/CN and T-XPB-CN samples.

chromatic light was obtained by passing light from a 500-W Xenon lamp (CHF XQ500W) through a double prism monochromator (SBP300). Photoluminescence (PL) spectroscopy analysis of the samples was performed using a spectrofluorophotometer (PELS 55) at an excitation wavelength of 390 nm.

2.3. Photocatalytic activity measurements

To investigate the photocatalytic activity of the fabricated nanocomposites, photocatalytic experiments for 2,4-DCP degradation and CO_2 reduction were performed. In a typical photocatalytic experiment for 2,4-DCP degradation, a 150-W Xenon lamp was selected as the light source, and 0.1 g of the photocatalyst and 20 mL of 10 mg/L 2,4-DCP aqueous solution were mixed by stirring for 1 h in an open glass reactor under light irradiation. The distance between the light source and reactor was 10 cm. After centrifugation, the concentrations of 2,4-DCP were analyzed at the characteristic optical absorption of 285 nm of 2,4-DCP using a Shimadzu UV-2550 spectrophotometer.

In a typical photocatalytic experiment for CO_2 reduction, 0.2 g of the powder sample was dispersed in a cylindrical steel reactor (volume of 100 mL and area of 3.5 cm^2) containing 3 mL of water. A 300-W Xenon lamp was used as the light source. High-purity CO_2 gas was passed through the water and then entered into the reaction setup to reach ambient pressure. The photocatalyst was allowed to equilibrate in the $\text{CO}_2/\text{H}_2\text{O}$ system for 1 h. During irradiation, approximately 0.5 mL of gas was continually removed from the reaction cell at a given time interval for gas chromatography analyses of the CO and O_2 (GC-7900, thermal conductivity detector, molecular sieve 0.5 nm, N_2 carrier, Techcomp, China) and CH_4 (GC-2014, flame ionization detector, molecular sieve 0.5 nm, N_2 carrier, Shimadzu Corp, Japan) concentrations.

3. Results and discussion

3.1. Structural characterization

XRD patterns of the P-O bridged $\text{TiO}_2/\text{g-C}_3\text{N}_4$ composites

are presented in Fig. 1(a). The phase composition, peak intensity, and half-peak width did not change after introducing different amounts of phosphate groups, implying that the phosphate modification did not affect the crystal phase composition, crystallite size, or crystallinity of the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ nanocomposites. The DRS spectra (Fig. 1(b)) indicate that the light absorption and band gap were unchanged before and after the phosphate groups were introduced. In addition, the TEM images (Fig. 2(a)) reveal nano- TiO_2 dispersed on the surfaces of slice-like $\text{g-C}_3\text{N}_4$; their morphology was not affected after phosphate modification. Noticeably, heterojunctions were formed between TiO_2 and $\text{g-C}_3\text{N}_4$, as shown in the high-resolution TEM (HRTEM) image in Fig. 2(b), in which facet distances of 0.336 and 0.35 nm (attributed to $\text{g-C}_3\text{N}_4$ (002) and TiO_2 (101), respectively) are observed [10]. The characteristic peaks appearing at 1235, 1322, 1423, 1572, 1640, and 806 cm^{-1} in the FTIR spectra (Fig. 3) are assigned to $\text{g-C}_3\text{N}_4$. In addition, the band at approximately 3430 cm^{-1} corresponds to physically absorbed H_2O or $-\text{OH}$ [23]. Notably, as observed in the inset of Fig. 3, a new FTIR peak appeared at approximately 1050 cm^{-1} after the phosphate group was introduced, which is attributed to the P-O group [25], and its intensity gradually increased with increasing phosphate group addition. Therefore, it is deduced that the P-O linkers are built as bridges in the formed heterojunction between TiO_2 and $\text{g-C}_3\text{N}_4$. It is generally acceptable that the built P-O bridges could connect to TiO_2 and

Fig. 2. TEM images of T/CN (a) and T-10PB-CN (b) (the inset shows a HRTEM image of T-10PB-CN).

Fig. 3. FTIR spectra of CN, T/CN, and T-10PB-CN (the inset show the FTIR spectra of T-XPB-CN).

g-C₃N₄ via surface OH groups [24]. This built 'P-O bridge' would improve the connection of TiO₂ and g-C₃N₄ in the fabricated nanocomposites, which is favorable for charge transfer and separation.

3.2. Photogenerated charge properties

SS-SPS is a reliable and sensitive technique to directly explore the properties of photogenerated charge separation of semiconductors [26]. The SS-SPS response mainly results from the photogenerated charge separation via the diffusion process in semiconductors [27]. As observed in the inset of Fig. 4(a), the SS-SPS responses of the TiO₂/g-C₃N₄ nanocomposites were enhanced after the introduction of different amounts of phosphate groups, especially for T-10PB-CN, mainly because the appropriate amount of phosphate is favorable for charge transfer. Notably, the SS-SPS response in N₂ atmosphere generally reflects the actual charge separation between heterojunctions. As observed in Fig. 4(a), T/CN exhibits an obvious SS-SPS response in N₂ atmosphere, whereas no SS-SPS response was

observed for CN, implying that the transfer process of photo-generated electrons from g-C₃N₄ to TiO₂ occurs to promote charge separation. As expected, T-10PB-CN exhibited the strongest SS-SPS response, indicating that the built P-O bridges are favorable for charge transfer and separation by improving the connection between TiO₂ and g-C₃N₄.

The PL spectra are presented in Fig. 4(b). The PL peak intensity of CN decreased after coupling with an appropriate amount of TiO₂ (T/CN), especially for T-10PB-CN, which is in good agreement with the SS-SPS results. This finding demonstrates that the photogenerated carrier recombination of CN was gradually decreased by coupling with TiO₂ and by introducing P-O functional bridges.

3.3. Photocatalytic activities

The photogenerated charge separation of g-C₃N₄ was enhanced by coupling with an appropriate amount of nano-TiO₂, especially with the P-O bridged TiO₂. Thus, the P-O bridged TiO₂/g-C₃N₄ nanocomposites were expected to exhibit enhanced photocatalytic activities compared with bare g-C₃N₄ and T/CN nanocomposites. To investigate the photocatalytic activity of the nanocomposites, photocatalytic experiments for the degradation of 2,4-DCP were performed. As expected, T/CN exhibited higher photocatalytic activity than CN for the degradation of 2,4-DCP (Fig. 5(a)), and the photocatalytic activity was further enhanced upon coupling with different amounts of P-O bridged TiO₂. In addition, T-10PB-CN exhibited the highest activity, which was approximately 1.6-times and 3.0-times higher than those of T/CN and CN, respectively. The circulatory experiments indicate that the P-O bridges in the TiO₂/g-C₃N₄ nanocomposite were stable during the photocatalytic reactions.

The prepared nanocomposites also exhibited excellent photocatalytic activity for CO₂ reduction, as observed in Fig. 5 (b). CH₄ and O₂ were the main products detected with a small amount of CO, and the photocatalytic activity of T/CN for CO₂ reduction was clearly higher than that of pure CN, especially for T-10PB-CN. In addition, the activity of T-10PB-CN was ap-

Fig. 4. SS-SPS responses (a) in N₂ with the SS-SPS responses of T/CN and T-XPB-CN in air shown in the inset and PL spectra (b) of CN, T/CN, and T-10PB-CN.

Fig. 5. (a) First-order kinetic plots of 2,4-DCP degradation on CN, T/CN, and T-XPB-CN; (b) Photocatalytic activities for CO_2 conversion of CN, T/CN, and T-10PB-CN.

proximately 2.0 and 3.0 times those of T/CN and CN, respectively. Noticeably, the photocatalytic activity results are consistent with the SS-SPS responses, indicating that the photocatalytic activity mainly depends on the photogenerated charge separation.

3.4. Discussion

To further examine the enhanced photocatalytic activity mechanism of the P-O bridged $\text{TiO}_2/\text{g-C}_3\text{N}_4$ nanocomposites, isopropanol (IPA), benzoquinone (BQ), and ethylenediamine tetraacetic acid disodium salt (EDTA-2Na) were added to the system as scavenging species for the degradation of 2,4-DCP to investigate the generation and roles of active substance of $\cdot\text{OH}$, $\cdot\text{O}_2^-$, and h^+ , respectively. As observed in Fig. 6, the addition of BQ and EDTA-2Na did not obviously affect the photocatalytic activities of CN, T/CN, or T-10PB-CN. However, the photocatalytic activity was significantly inhibited with the addition of

Fig. 6. Photocatalytic degradation rates of 2,4-DCP in the presence of IPA, BQ, and EDTA-2Na after irradiation for 1 h on CN, T/CN, and T-10PB-CN.

IPA, suggesting that the $\cdot\text{OH}$ formed from the oxidation of photogenerated holes is the key species dominating the degradation of 2,4-DCP. Improving photogenerated charge separation is a highly feasible and effective approach to enhance the photocatalytic activity for the degradation of organic pollutants.

Based on these results, the mechanism illustrated in Fig. 7 was proposed. Coupling with an appropriate amount of nano- TiO_2 would improve photogenerated electron transfer from the conduction band of $\text{g-C}_3\text{N}_4$ to TiO_2 because of their suitable conduction band positions, thereby promoting the separation of photogenerated carriers so as to enhance the photocatalytic activity of $\text{g-C}_3\text{N}_4$. However, the performance of the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ nanocomposite remains unsatisfactory because of the poor connection between TiO_2 and $\text{g-C}_3\text{N}_4$. Hence, the phosphate group is introduced as a 'P-O bridge' to tightly connect TiO_2 and $\text{g-C}_3\text{N}_4$ so as to improve the separation of photogenerated carriers of $\text{g-C}_3\text{N}_4$. Consequently, the effective separation of photogenerated carriers could increase the amount of $\cdot\text{OH}$, which is produced by photogenerated holes oxidizing H_2O , to fundamentally enhance the photocatalytic activity for the degradation of 2,4-DCP.

Fig. 7. Schematic illustration of the transfer and separation of photo-generated charges in the P-O bridged $\text{TiO}_2/\text{g-C}_3\text{N}_4$ nanocomposite.

4. Conclusions

P–O bridged $\text{TiO}_2/\text{g-C}_3\text{N}_4$ nanocomposites were successfully prepared and utilized as photocatalysts for 2,4-DCP degradation and CO_2 reduction. The P–O functional bridges improved the heterojunction connection between TiO_2 and $\text{g-C}_3\text{N}_4$, thereby greatly enhancing the charge transfer and separation so as to result in promoted photocatalytic activity. In addition, the $\cdot\text{OH}$ formed from the oxidation of photogenerated holes is considered as the key species dominating the degradation of 2,4-DCP. This work provides a feasible strategy for the design and synthesis of high-performance $\text{g-C}_3\text{N}_4$ -based nanocomposite photocatalysts for pollutant degradation and CO_2 reduction.

References

- [1] G. H. Dong, K. Zhao, L. Z. Zhang, *Chem. Commun.*, **2012**, 48, 6178–6180.
- [2] B. Chai, T. Y. Peng, J. Mao, K. Li, L. Zan, *Phys. Chem. Chem. Phys.*, **2012**, 14, 16745–16752.
- [3] J. G. Yu, S. H. Wang, J. X. Low, W. Xiao, *Phys. Chem. Chem. Phys.*, **2013**, 15, 16883–16890.
- [4] K. Sridharan, E. Jang, T. J. Park, *Appl. Catal. B*, **2013**, 142, 718–728.
- [5] X. Zhou, J. Zou, S. Zhang, M. Pan, W. Y. Gong, *Chin. J. Catal.*, **2017**, 38, 287–295.
- [6] Z. X. Zeng, K. X. Li, K. Wei, Y. H. Dai, L. S. Yan, H. Q. Guo, X. B. Luo, *Chin. J. Catal.*, **2017**, 38, 498–508.
- [7] C. Wang, L. Y. Hu, M. Y. Wang, Y. H. Ren, B. Yue, H. Y. He, *Chin. J. Catal.*, **2016**, 37, 2003–2008.
- [8] S. B. Yang, Y. J. Gong, J. S. Zhang, L. Zhan, L. L. Ma, Z. H. Fang, R. Vajtai, X. C. Wang, P. M. Ajayan, *Adv. Mater.*, **2013**, 25, 2452–2456.
- [9] J. S. Zhang, J. H. Sun, K. Maeda, K. Domen, P. Liu, M. Antonietti, X. Z. Fu, X. C. Chen, *Energy Environ. Sci.*, **2011**, 4, 675–678.
- [10] L. Gu, J. Y. Wang, Z. J. Zou, X. J. Han, *J. Hazard. Mater.*, **2014**, 268, 216–223.
- [11] Y. J. Wang, R. Shi, J. Lin, Y. F. Zhu, *Energy Environ. Sci.*, **2011**, 4, 2922–2929.
- [12] R. Yin, Q. Z. Luo, D. S. Wang, H. T. Sun, Y. Y. Li, X. Y. Li, J. An, *J. Mater. Sci.*, **2014**, 49, 6067–6073.
- [13] G. Q. Li, N. Yang, W. L. Wang, W. F. Zhang, *J. Phys. Chem. C*, **2009**, 113, 14829–14833.
- [14] S. Tonda, S. Kumar, S. Kandula, V. Shnker, *J. Mater. Chem. A*, **2014**, 2, 6772–6780.
- [15] L. M. Sun, X. Zhao, C. J. Jia, Y. X. Zhou, X. F. Cheng, P. Li, L. Liu, W. L. Fan, *J. Mater. Chem.*, **2012**, 22, 23428–23438.
- [16] Z. L. Xu, C. S. Zhuang, Z. J. Zou, Z. Y. Wang, X. C. Xu, T. Y. Peng, *Nano Res.*, **2017**, DOI: 10.1007/s12274-017-1453-2.
- [17] C. Han, Y. D. Wang, Y. P. Lei, B. Wang, N. Wu, Q. Shi, Q. Li, *Nano Res.*, **2015**, 8, 1199–1209.
- [18] K. Pandiselvi, H. F. Fang, X. B. Huang, J. Y. Wang, X. C. Xu, T. Li, *J. Hazard. Mater.*, **2016**, 314, 67–77.
- [19] Y. L. Li, J. S. Wang, Y. L. Yang, Y. Zhang, D. He, Q. E. An, G. Z. Cao, *J. Hazard. Mater.*, **2015**, 292, 79–89.
- [20] Z. J. Li, L. M. He, L. Q. Jing, J. S. Lin, Y. B. Luan, *Chem. Plus. Chem.*, **2013**, 78, 670–676.
- [21] M. Z. Xie, Y. J. Feng, X. D. Fu, P. Luan, L. Q. Jing, *J. Alloys. Compd.*, **2015**, 631, 120–124.
- [22] X. D. Fu, M. Z. Xie, P. Luan, L. Q. Jing, *J. ACS. Appl. Mater. Interfaces*, **2014**, 6, 18550–18558.
- [23] F. Raziq, C. M. Li, M. Humayun, Y. Qu, A. Zada, H. T. Yu, L. Q. Jing, *Mater. Res. Bull.*, **2015**, 70, 494–499.
- [24] L. Q. Jing, X. Qin, Y. B. Luan, Y. C. Qu, M. Z. Xie, *J. Appl. Surf. Sci.*, **2012**, 8, 3340–3349.
- [25] C. Liu, L. Q. Jing, L. M. He, Y. B. Luan, C. M. Li, *Chem. Commun.*, **2014**,

Graphical Abstract

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Synthesis of $\text{TiO}_2/\text{g-C}_3\text{N}_4$ nanocomposites with phosphate–oxygen functional bridges for improved photocatalytic activity

Chong Liu, Fazal Raziq, Zhijun Li, Yang Qu, Amir Zada, Liqiang Jing*
Heilongjiang University; Heilongjiang University of Science and Technology

The introduced phosphate groups tightly contact TiO_2 and $\text{g-C}_3\text{N}_4$ like a P–O bridge, which is helpful for the effective transfer of photogenerated electrons from $\text{g-C}_3\text{N}_4$ to TiO_2 , thereby the lifetime and separation of photogenerated charges are further improved, consequently leading to the enhanced photocatalytic activities for $\text{TiO}_2/\text{g-C}_3\text{N}_4$ nanocomposites.

50, 1999–2001.

[26] L. Kronik, Y. Shapira, *Surf. Sci. Rep.*, **1999**, 37, 1–206.[27] H. L. Zhou, Y. Q. Qu, T. Zeid, X. F. Duan, *Energy Environ. Sci.*, **2012**, 5, 6732–6743.

高光催化活性的磷氧桥连TiO₂/g-C₃N₄纳米复合体的合成

刘 翀^{a,b}, Fazal Raziq^a, 李志军^a, 曲 阳^a, Amir Zada^a, 井立强^{a,*}^a黑龙江大学功能无机材料化学重点实验室, 黑龙江哈尔滨150080^b黑龙江科技大学环境与化工学院, 黑龙江哈尔滨150027

摘要: 石墨型氮化碳(g-C₃N₄)是一种新型非金属聚合物半导体材料,具有合理的能带结构、较好的稳定性及卓越的表面性质,因而受到了人们的广泛关注。目前,它作为光催化剂在降解污染物、光催化分解水产氢和光催化还原CO₂方面正呈现出巨大的应用潜力。然而,g-C₃N₄可见光响应范围窄、比表面积较小、尤其是光生载流子易复合等缺陷制约着其光催化活性的进一步提高。针对以上问题,人们对g-C₃N₄进行了大量的改性研究,其中构建能级匹配的纳米半导体/g-C₃N₄异质结复合体是常用的有效改善g-C₃N₄光生电荷分离进而提高其光催化活性的手段。但现有相关文献往往忽略了复合体界面接触情况对光生电荷转移和分离的影响,从而在一定程度上影响对光催化性能的改善。本课题组前期工作表明,通过磷氧、硅氧功能桥的建立可加强TiO₂/Fe₂O₃, ZnO/BiVO₄纳米复合物的界面接触,从而促进光生电荷的迁移和分离,进而进一步提高纳米复合体的光催化活性。这样,通过构建磷氧桥有望改善TiO₂和g-C₃N₄的紧密连接,以促进光生电子由g-C₃N₄向TiO₂的迁移、改善光生载流子的分离,进而更加显著地提高g-C₃N₄的光催化活性。但是相关工作至今尚未见到报道。

为此,本文通过简单的湿化学法成功地合成了磷氧(P–O)桥连的TiO₂/g-C₃N₄纳米复合体,并研究了P–O功能桥对TiO₂/g-C₃N₄纳米复合体光生电荷分离及其对光催化降解污染物及还原CO₂活性的影响。结果表明,g-C₃N₄与适量的纳米TiO₂复合,尤其是g-C₃N₄与适量P–O桥连TiO₂的复合可进一步提高g-C₃N₄的光催化活性。基于气氛调控的表面光电电压谱和光致发光谱等的分析,P–O桥连可促使g-C₃N₄的光生电子由g-C₃N₄向TiO₂转移,极大地促进了g-C₃N₄的光生电荷分离,因而使纳米复合体光催化活性大幅提高,其光催化降解2,4-DCP及还原CO₂活性均为g-C₃N₄的3倍。此外,自由基捕获实验表明,·OH作为空穴调控的直接中间产物,其对2,4-DCP的降解起主导作用。

关键词: TiO₂/g-C₃N₄纳米复合体; 磷氧桥; 电荷转移及分离; 光催化; 二氧化碳转化

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*通讯联系人. 电话/传真: (0451)86604760; 电子信箱: jinglq@hlju.edu.cn

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