available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

One-step synthesis of graphitic carbon nitride nanosheets for efficient catalysis of phenol removal under visible light

Wang Ding, Suqin Liu *, Zhen He

College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, Hunan, China

ARTICLE INFO

Article history:

Received 21 April 2017

Accepted 30 July 2017

Published 5 October 2017

Keywords:

g-C₃N₄ nanosheet

Phenol degradation

Polymer

Semiconductor

Photocatalyst

ABSTRACT

Graphitic carbon nitride (g-C₃N₄) nanosheet photocatalysts were synthesized via a facile impregnation-thermal method. The as-prepared materials were characterized and investigated as metal-free photocatalysts for the degradation of phenol in aqueous solution under visible light. Results revealed that the g-C₃N₄ nanosheets exhibited a 78.9% degradation for phenol after 30 min, which was much faster than that of the pristine g-C₃N₄. Using Brunauer-Emmett-Teller theory, the surface area of g-C₃N₄ nanosheets was 103.24 m²/g, which was much larger than that of g-C₃N₄. The larger surface area increases the contact area of the material with phenol, enhancing the photocatalytic activity. These results highlight the potential application of sustainable metal-free photocatalysts in water purification.

© 2017, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

The field of heterogeneous photocatalysis has developed rapidly in the last four decades as governments and scientists research green and sustainable technologies [1,2]. Semiconductor-based photocatalysis requires only light as a driving force. A suitable semiconductor as a photocatalyst has been used in catalytic reactions for a variety of applications, such as hydrogen production from water splitting [3], CO₂ reduction into hydrocarbon fuels [4], decomposition and mineralization of organic pollutants [5], selective organic synthesis [6], and disinfection of bacteria [7]. Semiconductor-based photocatalysis has emerged with valuable metal-based semiconductors; however, they are active only in the ultraviolet region and have moderate performances.

Graphitic carbon nitride (g-C₃N₄) is the most stable allotrope among various carbon nitrides (CNs) under ambient conditions. Unlike TiO₂, which is only active in the UV region, g-C₃N₄ possesses a bandgap of ca. 2.7 eV [8,9], which enables it

to be a visible-light active photocatalyst for a range of reactions. More importantly, g-C₃N₄ is only composed of two earth-abundant elements: carbon and nitrogen, suggesting that it can be easily prepared at low cost [10,11]. Moreover, its polymeric nature allows control over the surface chemistry via molecular-level modification and surface engineering. The unique aforementioned characteristics of g-C₃N₄ make this material a very promising photocatalyst for various applications [12]. Great and fruitful efforts have been made on g-C₃N₄-based photocatalysis [13]. However, pristine g-C₃N₄ still suffers from unsatisfactory photocatalytic efficiency because of its restricted visible-light harvesting capacity, ready recombination of charge carriers, and low surface area [13–21].

Many researchers have put great effort of preparing g-C₃N₄ nanostructures (synthetic routes [22–24], thermal exfoliation [25–27], and templates [28]). For example, Shalom et al. [23] reported a new and simple synthetic pathway to form ordered, hollow CN structures, using a cyanuric acid-melamine complex in ethanol as a starting product. Yang et al. [24] demonstrated a

* Corresponding author. Tel: +86-15307317737; E-mail: sqliu2003@126.com

DOI: 10.1016/S1872-2067(17)62907-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 10, October 2017

biotic precursor approach of g-C₃N₄ polymers synthesized from urea and nucleobases. Yang et al. [27] reported a facile and green approach to prepare few-layered polymeric CN semiconductors by a one-step carbon/nitrogen steam reforming reaction. g-C₃N₄ can be imprinted with a twisted hexagonal rod-like morphology by a nanocasting technique using chiral silicon dioxides as templates [28]. Ou et al. [29] fabricated crystalline CN nanosheets by exfoliation of bulk tri-s-triazine-based crystalline CN powder in isopropanol via sonication for 15 h. Guo et al. [30] presented a facile synthesis method (the mixture of glucose, boric acid and urea) to produce a porous structure of two-dimensional boron CN nanosheets. In the results of the above-mentioned studies, g-C₃N₄ exhibited dramatically enhanced visible-light photocatalytic activity toward hydrogen evolution and pollutant degradation. A potential scale method for preparing g-C₃N₄ nanosheets remains a challenge.

In this work, we developed a simple method to prepare g-C₃N₄ nanosheets by thermal polymerization of cyanuric acid and melamine in air. These g-C₃N₄ nanosheets may show superior photocatalytic activities compared with the bulk g-C₃N₄. The photocatalytic activity of g-C₃N₄ is evaluated toward phenol degradation under visible-light irradiation and compared with that of g-C₃N₄.

2. Experimental

2.1. Chemicals and materials

Melamine, cyanuric acid, phenol, and methanol were purchased from Sinopharm (Shanghai, China). All chemicals were of analytical grade and used without further purification. All aqueous solutions were freshly prepared with deionized water.

2.2. Synthesis of g-C₃N₄(x)

All g-C₃N₄ samples were synthesized using melamine and cyanuric acid as the starting material through a stage programming heating approach. The starting material was heated to 550 °C at a heating rate of 2 °C/min and held at this temperature for 4 h. The sample was denoted as g-C₃N₄(x), where x refers to the molar ratio of melamine and cyanuric acid.

For comparison, bulk g-C₃N₄ was prepared through a widely-used one-step polycondensation process. Briefly, 2 g of MA was directly heated to 550 °C in air and kept for 2 h.

2.3. Characterization

Scanning electron microscopy was performed with a FEI Nove NanoSEM 230 field emission system on loose and lightly pressed samples. X-ray diffraction patterns were measured on a Rigaku 2500 diffractometer with Cu-K α radiation ($\lambda = 0.15406$ nm) at a scan rate of 8°/min. X-ray photoelectron spectroscopy (XPS) spectra were obtained on a ThermoFisher-VG Scientific instrument with an Al-K α (1486.6 eV) monochromatic X-ray radiation (operated at 200 W) from a twin anode in the constant analyzer energy mode with an energy of 30 eV. The UV-vis absorption spectra were measured on a Shimadzu

UV2550 spectrophotometer using BaSO₄ as the reflectance standard.

2.4. Photocatalytic performance evaluation

Photodegradation of a phenol solution (50 mg/L) was performed to evaluate the photocatalytic performance of the synthesized catalysts in a top-window Pyrex cell with the temperature maintained at 20 °C by a circulating water system. The catalyst (50 mg) was added into the phenol solution (100 mL). Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min to ensure phenol adsorption/desorption equilibrium. The suspension was irradiated by a 300 W Xe lamp with a cut off filter (<400 nm) and an irradiation intensity of 100 mW/cm². At given time intervals, aliquots of the irradiated suspension were collected, centrifuged, and analyzed on a Shimadzu LC-20AT high-performance liquid chromatography system with an SPD-20A column. The detection wavelength was 280 nm. The mobile phase was a mixture of methanol and water with a volume ratio of 70:30 and a flow rate of 1 mL/min.

3. Results and discussion

The one-step pyrolysis of the precursor melamine showed decreased yields of the products as the molar ratio of melamine to cyanuric acid was varied from 1:0 to 1:9. Cyanuric acid is totally decomposed in these conditions. The appearance of the sample looked like messaline with characteristics associated with the delamination and crystal-structural alternation within the CN polymers [26,31].

Fig. 1 shows the scanning electron microscopy images of all samples. Many flakes with laminar morphologies were observed. However, the bulk g-C₃N₄ showed no exfoliation with irregular particles. The product after thermal exfoliation presented in Fig. 1 displayed a layer structure with some fabric-like surface. Fig. 2 shows a representative atomic force microscopy image of the g-C₃N₄(1:9) nanosheets. The lateral size of these sheets ranged from tens of nanometers to several micrometers. The thickness analysis of the nanosheets revealed a thickness of about 3.0 nm.

As cyanuric acid decomposed, the appearance of CN became mainly atomic layers with a thin, glossy, and transparent texture (Fig. 1). Moreover, from the detailed view of the sample, a distinct curved nanodomain was displayed at the edge of the large plane (Fig. 1). Such a structural distortion of 2D crystals has been demonstrated to stabilize the 2D structure, as also observed in single-layered graphene, which may be stabilized by the formation of finite-sized ripples [32,33].

Fig. 3 shows X-ray diffraction patterns of all the samples with a characteristic peak at 27.48° ($d = 0.326$ nm), corresponding to the (002) interlayer reflection of g-C₃N₄. The peak at 27.48° was weaker than those of the sample obtained by bulk polymerization at 550 °C, which indicated that the interlayer structure was destroyed after thermolysis. Moreover, the peak at 27.48° (attributed to the in-plane repeated tri-s-triazine units) become narrow with increased reaction temperature. The evolution of the curved shape and curls during the assem-

Fig. 1. Scanning electron microscopy images of g-C₃N₄ samples with different melamine:cyanuric acid ratios.

bly process in a fluidic medium may disturb the long-range packing of the tri-s-triazine rings (C₃N₃) in a layer along the (002) direction, as shown with the formation of the nanosheets topology at g-C₃N₄(1:9). The weak peak at 13.1° corresponds to the (100) plane, which is the in-plane structural packing of tri-s-triazine units caused by the decreased planar size of the layers during the thermal oxidation etching of bulk g-C₃N₄ [26].

The chemical structures of the samples were further ana-

lyzed by Fourier transform infrared spectroscopy, and the results are shown in Fig. 4. The broad peaks between 3000 and 3500 cm⁻¹ correspond to the N–H bond. The peaks in the region from 900 to 1800 cm⁻¹ are attributed to either trigonal C–N(–C)–C (full condensation) or bridging C–NH–C units, and these bands became sharp because of the ordered packing of hydrogen bonds in the long strands of polymeric melamine units after thermal oxidation etching in the layers of

Fig. 2. Atomic force microscopy images of g-C₃N₄(1:9), which is the sample with a molar ratio of melamine to cyanuric acid of 1:9.

Fig. 3. X-ray diffraction patterns of g-C₃N₄ samples of different melamine:cyanuric acid ratios.

Fig. 4. Fourier transform infrared spectra of g-C₃N₄ samples with different melamine:cyanuric acid ratios.

nanosheets. The peaks at 1251, 1325, 1419, 1571, and 1639 cm⁻¹ are the stretching modes of CN heterocycles. In addition, the characteristic breathing mode of triazine units at 810 cm⁻¹ was observed [34]. There were no differences of peaks between all samples, which indicated that the chemical structure of g-C₃N₄ (different molar ratios of melamine to cyanuric acid) was the same as that of bulk g-C₃N₄.

The optical absorption properties of the g-C₃N₄ were examined with UV-vis diffuse reflectance spectroscopy (Fig. 5). The texture evolution at the nanoscale can induce planar g-C₃N₄ warping spontaneously, and accordingly, an important modification of the optical absorption property [35,36]. As shown in Fig. 5, the samples exhibited one absorption edge around 450 nm in the blue region, which was identified as the intrinsic electronic transition from the HOCO-2 to LUCO in g-C₃N₄ polymers ($\pi \rightarrow \pi^*$ transitions). Because of the extended 2D electron

delocalization, the band edge slightly red-shifted at a high temperature [26,31,37].

Using Brunauer-Emmett-Teller theory, the surface area of g-C₃N₄(1:9) was estimated as 103.24 m²/g, which is much larger than those of g-C₃N₄ prepared from urea (≈ 58.0 m²/g) [38] and melamine (8.0 m²/g) [39]. The g-C₃N₄(1:9) exhibited an enhanced performance in pollutant removal, such as phenol. The g-C₃N₄(1:9) showed a higher adsorption capacity of phenol than that of the g-C₃N₄(all) in the first 30 min. However, the g-C₃N₄ cannot remove the pollutants after the adsorption equilibrium was reached at 3 h. The g-C₃N₄ with a low molar ratio of melamine to cyanuric acid showed a low adsorption capacity and photocatalytic degradation ability, indicating a low pollutant removal ability. Because of the simultaneously high adsorption capacity and photocatalytic degradation ability, the high molar ratio enhanced the performance of pollutant re-

Fig. 5. (a) The UV-vis diffuse reflectance spectroscopy of samples with different melamine:cyanuric acid ratios, and (b) the band gap evaluation from the plots of $(ah\nu)^{1/2}$ vs. $h\nu$ (a = absorbance, h = Planck constant, and ν = frequency).

Fig. 6. (a) N₂ adsorption-desorption isotherm of g-C₃N₄(1:9); (b) Adsorption of phenol over g-C₃N₄ composites with different molar ratios (C is the instantaneous concentration, C_0 means the starting concentration); (c) Photodegradation of phenol over g-C₃N₄ composites with different molar ratios; (d) Multiple photocatalytic reaction over g-C₃N₄(1:9); (e) Temporal evolution of total organic compound concentration in g-C₃N₄(1:0) (1) and g-C₃N₄(1:9) (2) under visible-light irradiation.

removal via a cooperative effect of adsorption and photocatalytic degradation, which was 10 times that of pure g-C₃N₄ (Fig. 6(c)). Photocatalyst stability is important in application, so the reusability of the g-C₃N₄(1:9) for phenol degradation was evaluated (Fig. 6(d)). Over five consecutive cycles, no obvious deactivation of the photocatalyst was observed. To further test the mineralization degree of phenol during the photodegradation process, the evolution of total organic compounds during light irradiation was investigated (Fig. 6(e)). About 91% of phenol was mineralized to CO₂ within 210 min with the g-C₃N₄(1:9), which is three times that of the g-C₃N₄(1:0) during the same period. This result indicates that the g-C₃N₄(1:9) has a much higher mineralization efficiency for phenol photodegradation than g-C₃N₄(1:0).

As shown in Fig. 7(a), the addition of benzoquinone (BQ) and isopropanol (IPA) caused a notable change in photodegradation efficiency, suggesting the importance of $\bullet\text{O}_2^-$ radicals and $\bullet\text{OH}$ radicals. The addition of ethylenediaminetetraacetic acid (EDTA) showed almost no effect on photodegradation efficiency, suggesting a low importance of h^+ radicals. The Mott-Schottky plot for the g-C₃N₄(1:9) in Fig. 7(b) is linear to a reverse potential of -1 V. The x-intercept of the Mott-Schottky plot indicates a flat band voltage of -0.96 V. The temporal evolution of phenol and the hydroxylated phenolic intermediates for the g-C₃N₄(1:9) in Fig. 7(c) suggest that the major photodegradation products are catechol and hydroquinone at the beginning. As shown in Fig. 7(d), the photogenerated holes in the valance band of g-C₃N₄ ($E_{\text{VB}} = +1.30$ V, vs. NHE) are incapable of oxidizing hydroxyl groups into $\bullet\text{OH}$ radicals

($E(\bullet\text{OH}/\text{OH}^-) = +1.99$ V, vs. NHE) because of the more negative valance band potential, suggesting that the observed $\bullet\text{OH}$ radicals were generated from the $\bullet\text{O}_2^-$ radicals by a photochemical reaction. When phenol molecules are adsorbed on the surface of excited g-C₃N₄ nanosheets, there is activation of the phenol molecules by reaction with an $\bullet\text{OH}$ radical. The hydroxyl radical shows electrophilic character and prefers to attack electron rich ortho or para carbon atoms of phenol, forming dihydroxycyclohexadienyl radicals that undergo further reaction with dissolved oxygen to yield dihydroxy benzenes with simultaneous generation of an $\bullet\text{OH}$ radical. Dihydroxycyclohexadienyl radicals are also converted to phenoxy radicals. These phenoxy radicals can react with $\bullet\text{OH}$ to form benzoquinone, hydroquinone, which are colored intermediates and also dihydroxy benzenes. The direct combination of two phenoxy radicals can form intermediates with two aromatic rings attached to each other by a single bond.

The synergy of adsorption and photocatalytic degradation by high temperature is further explored by photocurrent analysis. As shown in Fig. 8, a low photoelectric response of agar was observed. The photocurrent of low molar ratio cyanuric acid samples is similar to that of pure g-C₃N₄, whereas the high molar ratio cyanuric acid materials show an enhanced photoelectric response. Another interesting observation was the slow photocurrent response of the g-C₃N₄ sample during the on-off irradiation cycles. Upon light irradiation, the conduction band of the g-C₃N₄ sample serves as electron reservoirs to store the photogenerated electrons, so only a portion of the photoelectrons are transported to the back-contact electrode until the

Fig. 7. (a) Photodegradation efficiency of phenol with different trapping agent (BQ (benzoquinone, $\cdot O_2^-$), EDTA (ethylenediaminetetraacetic acid, h^+), and IPA (isopropanol, $\cdot OH$)); (b) Solid-state Mott-Schottky plots for g-C₃N₄(1:9) collected at a reverse bias with a frequency of 100 kHz and scan rate of 10 mV/s; (c) Temporal evolution of phenol and the hydroxylated phenolic intermediates in g-C₃N₄(1:9); (d) Photocatalytic mechanism of the g-C₃N₄(1:9); (e) Phenol photodegradation route.

equilibrium state is reached. Thus, a gradually rising photocurrent response occurs.

4. Conclusions

Structurally distorted CN polymers (g-C₃N₄(1:9)) were fabricated during the delamination process of the layers. The minimum band gap is sensitive to the configuration of the

g-C₃N₄. As a wide-range visible-light photocatalyst, buckled CN converts light (> 495 nm) to run chemical reactions such as phenol removal. The basic units and connecting mode of CN show no major alternation, but the charge separation is promoted because of the 2D buckled structure and high polycondensation. This paper provides a new and simple method to synthesize high-performance g-C₃N₄ nanosheets, which explores a new photocatalytic oxidation catalyst for environmen-

Fig. 8. Photocurrent responses of samples with different melamine:cyanuric acid ratios under visible-light irradiation.

tal remediation and energy conversion.

References

- [1] F. K. Kessler, Y. Zheng, D. Schwarz, C. Merschjann, W. Schnick, X. C. Wang, M. J. Bojdys, *Nat. Rev. Mater.*, **2017**, 2, 17030.
- [2] Y. Zheng, L. H. Lin, B. Wang, X. C. Wang, *Angew. Chem. Int. Ed.*, **2015**, 54, 12868–12884.
- [3] A. Kudo, Y. Miseki, *Chem. Soc. Rev.*, **2009**, 38, 253–278.
- [4] S. N. Habisreutinger, L. Schmidt-Mende, J. K. Stolarczyk, *Angew. Chem. Int. Ed.*, **2013**, 52, 7372–7408.
- [5] D. Chatterjee, S. Dasgupta, *Photochem. Photobiol. C*, **2005**, 6, 186–205.
- [6] X. B. Chen, S. H. Shen, L. Guo, S. S. Mao, *Chem. Rev.*, **2010**, 110, 6503–6570.
- [7] X. J. Lang, X. D. Chen, J. C. Zhao, *Chem. Soc. Rev.*, **2014**, 43, 473–486.
- [8] X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.*, **2009**, 8, 76–80.
- [9] S. C. Yan, S. B. Lü, Z. S. Li, Z. G. Zou, *Dalton Trans.*, **2010**, 39, 1488–1491.
- [10] Y. Zheng, J. Liu, J. Liang, M. Jaroniec, S. Z. Qiao, *Energy Environ. Sci.*, **2012**, 5, 6717–6731.
- [11] X. C. Wang, S. Blechert, M. Antonietti, *ACS Catal.*, **2012**, 2, 1596–1606.
- [12] Z. W. Zhao, Y. J. Sun, F. Dong, *Nanoscale*, **2015**, 7, 15–37.
- [13] R. Godin, Y. Wang, M. A. Zwiijnenburg, J. W. Tang, J. R. Durrant, *J. Am. Chem. Soc.*, **2017**, 139, 5216–5224.
- [14] J. S. Zhang, J. H. Sun, K. Maeda, K. Domen, P. Liu, M. Antonietti, X. Z. Fu, X. C. Wang, *Energy Environ. Sci.*, **2011**, 4, 675–678.
- [15] T. Sano, S. Tsutsui, K. Koike, T. Hirakawa, Y. Teramoto, N. Negishi, K. Takeuchi, *Mater. Chem. A*, **2013**, 1, 6489–6496.
- [16] S. W. Cao, J. G. Yu, *J. Phys. Chem. Lett.*, **2014**, 5, 2101–2107.
- [17] Y. J. Cui, Z. X. Ding, P. Liu, M. Antonietti, X. Z. Fu, X. C. Wang, *Phys. Chem. Chem. Phys.*, **2012**, 14, 1455–1462.
- [18] S. C. Yan, Z. S. Li, Z. G. Zou, *Langmuir*, **2010**, 26, 3894–3901.
- [19] Z. H. Lin, G. Cheng, L. Lin, S. Lee, Z. L. Wang, *Angew. Chem. Int. Ed.*, **2013**, 52, 12545–12549.
- [20] G. H. Dong, K. Zhao, L. Z. Zhang, *Chem. Commun.*, **2012**, 48, 6178–6180.
- [21] J. H. Li, B. Shen, Z. H. Hong, B. Z. Lin, B. F. Gao, Y. L. Chen, *Chem. Commun.*, **2012**, 48, 12017–12019.
- [22] X. J. Bai, S. C. Yan, J. J. Wang, L. Wang, W. J. Jiang, S. L. Wu, C. P. Sun, Y. F. Zhu, *J. Mater. Chem. A*, **2014**, 2, 17521–17529.
- [23] M. Shalom, S. Inal, C. Fettkenhauer, D. Neher, M. Antonietti, *J. Am. Chem. Soc.*, **2013**, 135, 7118–7121.
- [24] C. Yang, B. Wang, L. Z. Zhang, L. Yin, X. C. Wang, *Angew. Chem. Int. Ed.*, **2017**, 56, 6627–6631.
- [25] Y. N. Li, M. Q. Wang, S. J. Bao, S. Y. Lu, M. W. Xu, D. B. Long, S. H. Pu, *Ceram. Int.*, **2016**, 42, 18521–18528.
- [26] P. Niu, L. Zhang, G. Liu, H. M. Cheng, *Adv. Funct. Mater.*, **2012**, 22, 4763–4770.
- [27] P. J. Yang, H. H. Ou, Y. Fang, X. C. Wang, *Angew. Chem. Int. Ed.*, **2017**, 56, 3992–4770.
- [28] Y. Zheng, L. H. Lin, X. J. Ye, F. S. Guo, X. C. Wang, *Angew. Chem. Int. Ed.*, **2014**, 53, 11926–11930.
- [29] H. H. Ou, L. H. Lin, Y. J. Zheng, P. X. Yang, Y. X. Fang, X. C. Wang, *Adv. Mater.*, **2017**, 29.
- [30] F. S. Guo, P. J. Yang, Z. M. Pan, X. N. Cao, Z. L. Xie, X. C. Wang, *Angew. Chem. Int. Ed.*, **2017**, 56, 8231–8235.
- [31] X. D. Zhang, X. Xie, H. Wang, J. J. Zhang, B. C. Pan, Y. Xie, *J. Am. Chem. Soc.*, **2013**, 135, 18–21.
- [32] J. M. Carlsson, *Nat. Mater.*, **2007**, 6, 801–802.
- [33] A. Fasolino, J. H. Los, M. I. Katsnelson, *Nat. Mater.*, **2007**, 6, 858–861.

Graphical Abstract

Chin. J. Catal., 2017, 38: 1711–1718 doi: 10.1016/S1872-2067(17)62907-3

One-step synthesis of graphitic carbon nitride nanosheets for efficient catalysis of phenol removal under visible light

Wang Ding, Suqin Liu*, Zhen He
Central South University

A simple method was developed to prepare g-C₃N₄ nanosheets by thermal polymerization of cyanuric acid and melamine in air. The g-C₃N₄ nanosheets showed superior photocatalytic activities than bulk g-C₃N₄.

- [34] A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J. O. Müller, R. Schlögl, J. M. Carlsson, *Mater. Chem.*, **2008**, 18, 4893–4770.
- [35] A. B. Jorge, D. J. Martin, M. T. S. Dhanoa, A. S. Rahman, N. Makwana, J. Tang, A. Sella, F. Corà, S. Firth, J. A. Darr, P. F. Müller, *J. Phys. Chem. C*, **2013**, 117, 7178–7185.
- [36] Y. A. Li, J. S. Zhang, Q. S. Wang, Y. X. Jin, D. H. Huang, Q. L. Cui, G. T. Zou, *J. Phys. Chem. B*, **2010**, 114, 9429–9434.
- [37] J. H. Sun, J. S. Zhang, M. W. Zhang, M. Antonietti, X. Z. Fu, X. C. Wang, *Nat. Commun.*, **2012**, 3, 2152/1–2152/7.
- [38] G. G. Zhang, J. S. Zhang, M. W. Zhang, X. C. Wang, *J. Mater. Chem.*, **2012**, 22, 8083–8091.
- [39] S. C. Yan, Z. S. Li, Z. G. Zou, *Langmuir*, **2009**, 25, 10397–10401.

一步法合成g-C₃N₄纳米片用作苯酚可见光降解高效催化剂

丁 望, 刘素琴*, 何 震

中南大学化学化工学院, 湖南长沙410083

摘要: 石墨相氮化碳(g-C₃N₄)是一种在室温条件下最稳定的氮化碳。同时g-C₃N₄的带隙为2.7 eV, 可以利用可见光催化很多反应, 例如光解水、CO₂还原、有机污染物降解和有机物合成。但普通体相g-C₃N₄的光催化性能不尽如人意, 主要是由于普通体相材料的载流子复合效率高, 可见光(<450 nm)利用率低且比表面积小。众所周知, 半导体的光催化性能与材料表面状态密切相关, 因此可以控制合成条件来制备有利于光催化形貌的g-C₃N₄材料。普通体相g-C₃N₄材料的比表面积较小, 约为10 m²/g, 导致传质作用较差, 光生电子-空穴复合严重, 因此制备高比表面积的g-C₃N₄材料是目前研究的热点。我们发现在550 °C下将三聚氰胺和三聚氰酸一起煅烧可以一步热合成g-C₃N₄纳米片, 合成温度较低, 对材料带隙影响小, 同时可以提高材料比表面积, 从而极大地提高了材料的光降解苯酚性能。

XRD测试发现, 随着前驱体中三聚氰酸比例增加, 材料的主峰从27.38°显著偏移至27.72°。这表明三嗪环面内相连构成CN平面, 同时CN层也会有堆叠最终形成g-C₃N₄材料。通过BET测试, g-C₃N₄纳米片的比表面积为103.24 m²/g。采用AFM分析得到g-C₃N₄纳米片的厚度为3.07 nm。研究了该g-C₃N₄纳米片的光降解性能, 结果显示, 在可见光照射30 min后, 使用这种g-C₃N₄纳米片作为催化剂的条件下, 苯酚降解率达到最优的81%。在5次循环利用后, g-C₃N₄(1:9)的降解率还能保持在80%以上, 说明材料有良好的循环稳定性。这主要得益于材料的纳米片结构, 在对苯酚吸附时不会有很复杂的吸附与脱附过程。同时纳米片结构可为有机污染物的吸附和原位降解提供传质通道。光反应体系中的产物由HPLC检测, 分析苯酚的降解产物及产物的产量可以大致推测苯酚可能的降解历程。

在三聚氰酸作用下, CN聚合层弯曲, 减少了CN层之间的相互结合, 同时不会对材料的带隙产生影响。同时整个合成过程无需引发剂, 也不会导致CN层的基本单元和连接方式发生改变, 同时由于二维片层结构, 提高了材料的电荷分离效率。通过苯酚的降解实验得知三聚氰胺与三聚氰酸的比例为1:9, 在550 °C下煅烧得到的g-C₃N₄纳米片的光降解性能最优, 同时具有很好的催化稳定性。

关键词: 石墨相氮化碳纳米片; 苯酚降解; 聚合物; 半导体; 光催化剂

收稿日期: 2017-04-21. 接受日期: 2017-07-30. 出版日期: 2017-10-05.

*通讯联系人. 电话: 15307317737; 电子信箱: sqliu2003@126.com

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).