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Preparation and photo-degradation performance of composite catalysts

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Abstract. Through facile mixing and heating method, g-C₃N₄ and ZnO organic-inorganic composite with varying the content of g-C₃N₄ has been synthesized. The composite catalysts were characterized by X-ray diffraction, BET surface area measurements and etc. The activity of composite photocatalyst g-C₃N₄-ZnO with 50% or 70% g-C₃N₄ for photo-degradation of MO is higher than that of either single-phase g-C₃N₄ or ZnO under visible light irradiation. Due to the enhancement of electron-hole separation, the as-prepared organic-inorganic composite exhibits an improved photo-degradation performance.

1. Introduction

In recent years, by using solar energy, the photocatalysis technique has a promising application for water splitting for hydrogen generation, removal of contamination and also photoreduction of CO₂ into fuels. Under light irradiation, the photogenerated electron-hole pairs which gives rise to the photooxidation-reduction reaction transfer to the surface of semiconductor[1]. While, to obtain highly efficient and low-cost photocatalysts is the key factor to realize the technique for large-scale industrial application. So far, to improve the photocatalytic performance of the photocatalyst, various techniques, such as element doping[2], loading cocatalyst[3] increasing surface area[4], and forming solid solution[5] were studied.

Zinc oxide (ZnO) has recently attracted considerable attention as a versatile material in a wide range of applications, including catalysis, piezoelectronic devices, actuators, photodetectors, light-emitting diodes, photoelectrochemical cells, biosensor and so forth.[6,7] ZnO is also expected as a good photocatalyst used in environmental purification. Recently, it has been documented that these applications depend greatly on their microstructures, including orientation, crystal size, and morphological characters.[8] ZnO materials with different morphologies, such as belts, rods, combs, cables, wires, tetrapods, and hierarchical nanostructures with high symmetries[6,9] have been synthesized. Many strategies are proposed to get various ZnO nanostructures, such as the vapor transport process using catalyst[10] or wet-chemistry route[11], and catalyst-free[12]. Hydrothermal or solvothermal techniques in the existing synthetic routes have been widely used to be the effective approaches for the facile operation, mild synthesis conditions and flexible adjustment of experimental parameters[13], which factors make such strategies more economic than vapor phase route.

Recently, graphite-like carbon nitride (g-C₃N₄), an organic polymer photocatalyst, has been reported [14], which possesses the removal of pollutants [15] and the performance of hydrogen or oxygen



production from water splitting under visible light irradiation, and such low-cost photocatalysts have potential application in the field of civil engineering. The simple polymer catalyst in photocatalysis field may have potential applications if some methods can be found for improving the photocatalytic activity of this catalyst. Some composite catalysts have shown better catalytic activity than that of single component catalyst, e.g., g-C₃N₄ and TaON composite photocatalyst was synthesized and showed better photocatalytic activity for photodegradation than single g-C₃N₄ or TaON[16]; Other composite photocatalysts such as g-C₃N₄-SrTiO₃:Rh[17], g-C₃N₄/Bi₂WO₆[18], MWNTs/g-C₃N₄[19] have been synthesized. For photocatalytic H₂ evolution under visible light irradiation, g-C₃N₄ and TiO₂ composite showed better performance than g-C₃N₄ or TiO₂[20]. Furthermore, as an efficient photocatalyst for photoreduction of CO₂, in situ synthesis of graphitic carbon nitride (g-C₃N₄)-N-TiO₂ heterojunction has been reported[21]. Therefore, through forming composite photocatalysts, it is expected to further improve the photocatalytic activity of g-C₃N₄.

Using simple mixing-heating method to prepare the g-C₃N₄ and ZnO composite and studying the photo-degradation of MO has been studied in this paper, and g-C₃N₄ and ZnO composite photocatalysts with varying the content of g-C₃N₄ were prepared. Based on the experimental results, the possible mechanism for the improved photocatalytic activity in photo-degradation of MO was proposed.

2. Experimental

The starting materials utilized are zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, analysis purity grade), 26~28% NH₃·H₂O, absolute ethanol (Nanjing Chemical Reagent Co. Ltd.). Poly(styrene sulfonic acid) sodium salt (PSS, MW = 300,000, Product no. 25704-18-1) was purchased from Alfa Aesar and used as received without further purification. Distilled water was used throughout the experiment.

In a typical process, Zn(NO₃)₂·6H₂O and PSS was dissolved in the solution containing water and ethanol with a proportion, then the NH₃·H₂O was dropped in it at room temperature. The mixture was stirred for 15 min, then transferred into Teflon-lined stainless steel autoclave, and heated at 120 °C for 5 h. These samples were treated by centrifugation and thoroughly rinsed with water and ethanol several times, and then dried at 60 °C in an oven for subsequent characterization. The photocatalyst of g-C₃N₄ was prepared by directly heating melamine at 500 °C (heating rate: 20 °C/min) for 2 h, and the further deammonation treatment was set at 520 °C for 2 h^[15], respectively in the semiclosed system to prevent sublimation of melamine. The as-prepared ZnO and g-C₃N₄ powder were mixed by ball-milling and then calcined at 400 °C for 2 h in a muffle furnace.

Characterization of samples: The products were characterized by X-ray diffraction (XRD) for phase identification on a Rigaku Ultima III diffractometer with Cu K α radiation ($\lambda = 0.154$ nm, 40 kV, 40 mA) and a scan rate of 10 °·min⁻¹. The specific surface area of the as-prepared powders was obtained on a Micromeritics TriStar 3000 instrument (USA) at 77 K and Brunauer–Emmett–Teller (BET) equation were used to calculate the specific surface area. Ultraviolet visible (UV-vis) diffuse reflection spectra were measured using a UV-vis spectrophotometer (Shimadzu UV-2550, Japan) and converted from reflection to absorbance by the Kubelka-Munk method.

The methyl orange (MO) dye was used to test the photocatalytic activities of as-prepared samples and the photocatalytic reaction was performed in a Pyrex reactor. The catalyst (0.1 g) was dispersed in 100 mL MO aqueous solution (4.2 mg L⁻¹). The light irradiation system contains a 300 W Xe lamp with cut-off filter L42 for visible light and a water filter to remove heating effects. The reaction solutions of the MO photodegradation for all experiments were first stirred in the dark for 1 h to reach the adsorption–desorption equilibrium of MO on catalysts. The MO degradation efficiency was evaluated using the UV-vis absorption spectra to measure the peak value of a maximum absorption of MO solution at wavelength of 463 nm.

3. Results and discussion

The TEM image provides further information on the morphology and crystalline structure. It can be observed from Figure 1, that porous ZnO plate is composed of nanocrystalline ZnO particles in about 10-50 nm and the pores are formed by the agglomeration of nanoparticles. The composite catalyst is

composed of porous ZnO and g-C₃N₄. And from the XRD result, the diffraction peaks are in good agreement with JCPDS No. 36-1451, a typical wurtzite-type ZnO crystal (hexagonal, *P6₃mc*). No impurity phases were detected.

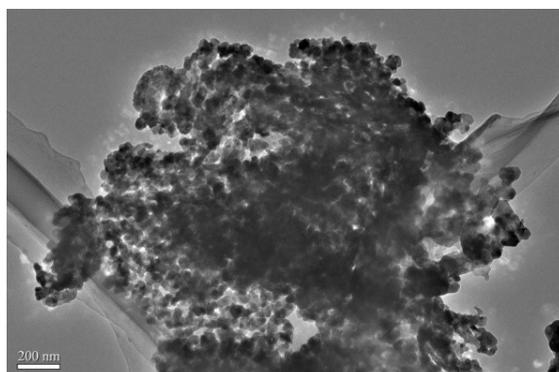


Figure 1. TEM image of the as-prepared g-C₃N₄ and ZnO composite photocatalyst.

To study the photo-degradation activity of g-C₃N₄ and ZnO composite photocatalyst, the pure g-C₃N₄, ZnO and g-C₃N₄ and ZnO organic–inorganic composite were used as photocatalysts for the degradation of MO. Figure 2 shows the degradation activities of MO over different photocatalysts under visible light irradiation. As shown in Figure 2, the 70 wt.% g-C₃N₄ and ZnO organic–inorganic composite show much higher activity than that of pure g-C₃N₄. This clearly indicates that the advantage of heating treatment is the formation of chemically bonded interfaces between the two materials, and the g-C₃N₄ and ZnO composite was determined as an efficient visible-light-driven photocatalyst for the degradation of MO.

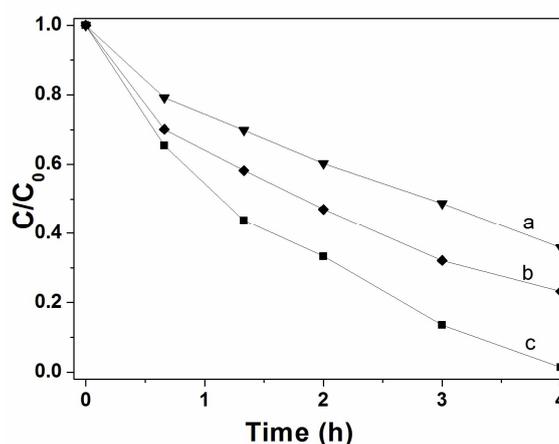


Figure 2. Comparison of MO degradation over different photocatalysts under visible light irradiation. a, g-C₃N₄; b, g-C₃N₄ and ZnO composite with 50% g-C₃N₄; c, g-C₃N₄ and ZnO composite with 70% g-C₃N₄.

4. Conclusion

In summary, the g-C₃N₄–ZnO composite materials with varying the content of g-C₃N₄ were prepared. Due to the effective separation of photogenerated electron-hole pairs by coupling ZnO, the photocatalytic result shows that the visible light-induced oxidation of MO rate with g-C₃N₄ was remarkably enhanced.

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References

- [1] J Schwitzgebel, J G Ekerdt, H Gerischer, *et al.* Role of the oxygen molecule and of the photogenerated electron in TiO₂-photocatalyzed air oxidation reactions. *The Journal of Physical Chemistry*, 1995, 99(15): 5633~5638.
- [2] Z G Zou, J H Ye, K Sayama, *et al.* Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst. *Nature*, 2001, 414(6864): 625~627.
- [3] S Sato, J M White. Photodecomposition of water over Pt/TiO₂ catalysts. *Chemical Physics Letters*, 1980, 72(1): 83~86.
- [4] F Bosc, A Ayrat, P A Albouy, *et al.* A simple route for low-temperature synthesis of mesoporous and nanocrystalline anatase thin films. *Chemistry of Materials*, 2003, 15(12): 2463~2468.
- [5] I Tsuji, H Kato, H Kobayashi, *et al.* Photocatalytic H₂ evolution under visible-light irradiation over band-structure-controlled (CuIn)_xZn_{2(1-x)}S₂ solid solutions. *Journal of Physical Chemistry B*, 2005, 109(15): 7323~7329.
- [6] M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, E. Weber, R. Russo and P. D. Yang, *Science*, 2001, 292, 1897.
- [7] Z. W. Zhao, X. J. Chen, B. K. Tay, J. S. Chen, Z. J. Han and K. A. Khor, *Biosens. Bioelectron.*, 2007, 23, 135.
- [8] J. G. Yu and X. X. Yu, *Environ. Sci. Technol.*, 2008, 42, 4902.
- [9] Z. W. Pan, Z. Dai and Z. L. Wang, *Science*, 2001, 291, 1947.
- [10] Z. L. Wang, *J. Mater. Chem.*, 2005, 15, 1021.
- [11] J. Zhang, S. R. Wang, M. J. Xu, Y. Wang, B. L. Zhu, S. M. Zhang, W. P. Huang and S. H. Wu, *Cryst. Growth Des.*, 2009, 9, 3532.
- [12] W. Ogasawara, W. Shenton, S. A. Davis and S. Mann, *Chem. Mater.*, 2000, 12, 2835.
- [13] B. Cheng and E. T. Samulski, *Chem. Comm.*, 2004, 8, 986.
- [14] X C Wang, K Maeda, A Thomas, *et al.* A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nature Materials*, 2009, 8(1): 76~80.
- [15] S C Yan, Z S Li, Z G Zou. Photodegradation performance of g-C₃N₄ fabricated by directly heating melamine. *Langmuir*, 2009, 25(17): 10397~10401.
- [16] S C Yan, S B Lv, Z S Li, *et al.* Organic-inorganic composite photocatalyst of g-C₃N₄ and TaON with improved visible light photocatalytic activities. *Dalton Transactions*, 2010, 39(6):1488~1491.
- [17] H W Kang, S N Lim, D S Song, *et al.* Organic-Inorganic Composite of g-C₃N₄-SrTiO₃: Rh Photocatalyst for Improved H₂ Evolution under Visible Light Irradiation[J]. *Inter. J. Hydro. Energy*, 2012, 37(16): 11602~11610.
- [18] L Ge, C C Han, J Liu, Novel Visible Light-Induced g-C₃N₄/Bi₂WO₆ Composite Photocatalysts for Efficient Degradation of Methyl Orange[J]. *Appl. Catal. B: Environ.*, 2011, 108-109: 100~107.
- [19] L Ge, C C Han. Synthesis of MWNTs/g-C₃N₄ Composite Photo-catalysts with Efficient Visible Light Photocatalytic Hydrogen Evolution Activity[J]. *Appl. Catal. B: Environ.*, 2012, 117-118: 268~274.
- [20] H J Yan, H X Yang. TiO₂-g-C₃N₄ composite materials for photocatalytic H₂ evolution under visible light irradiation. *Journal of Alloys and Compounds*, 2011, 509(4): L26~L29.
- [21] S Zhou, Y Liu, J M Li, *et al.* Facile in situ synthesis of graphitic carbon nitride (g-C₃N₄)-N-TiO₂ heterojunction as an efficient photocatalyst for the selective photoreduction of CO₂ to CO[J]. *Applied Catalysis B: Environmental*, 2014, 158-159: 20~29.