Chinese Journal of Catalysis 38 (2017) 1307–1314

available at www.sciencedirect.com

ScienceDirect

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

Article

Synthesis of graphene/tourmaline/TiO_2 composites with enhanced activity for photocatalytic degradation of 2-propanol

Lili Yin [a], Ming Zhao [a], Huilin Hu [a], Jinhua Ye [a,b,c], Defa Wang [a,b,*]

[a] *TJU-NIMS International Collaboration Laboratory, Key Laboratory of Advanced Ceramics and Machining Technology of Ministry of Education, Tianjin Key Laboratory of Composite and Functional Materials, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China*

[b] *Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China*

[c] *International Center of Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan*

ARTICLE INFO

Article history:
Received 29 December 2016
Accepted 28 January 2017
Published 5 August 2017

Keywords:
Photocatalysis
Graphene
Tourmaline
TiO_2
Composite
2-Propanol
Degradation

ABSTRACT

We report the construction of a graphene/tourmaline/TiO_2 (G/T/TiO_2) composite system with enhanced charge-carrier separation, and therefore enhanced photocatalytic properties, based on tailoring the surface-charged state of graphene and/or by introducing an external electric field arising from tourmaline. A simple two-step hydrothermal method was used to synthesize G/T/TiO_2 composites and poly(diallyldimethylammonium chloride)-G/T/TiO_2 composites. In the photocatalytic degradation of 2-propanol (IPA), the catalytic activity of the composite containing negatively charged graphene was higher than of the composite containing positively charged graphene. The highest acetone evolution rate (223 μmol/h) was achieved using the ternary composite with the optimum composition, i.e., G0.5/T5/TiO_2 (0.5 wt% graphene and 5 wt% tourmaline). The involvement of tourmaline and graphene in the composite is believed to facilitate the separation and transportation of electrons and holes photogenerated in TiO_2. This synergetic effect could account for the enhanced photocatalytic activity of the G/T/TiO_2 composite. A mechanistic study indicated that $O_2^{\bullet-}$ radicals and holes were the main reactive oxygen species in photocatalytic degradation of IPA.

1. Introduction

Photocatalysis using a semiconductor and solar light is widely regarded as an ideal green technique for dealing with the global energy crisis and environmental issues [1–5]. In recent decades, many researchers in the field of photocatalysis have focused their attention on improving the photocatalytic efficiency to enable practical applications [6–10]. The photocatalytic efficiency is influenced by many factors, among which the separation and transportation of photoexcited charge carriers (electrons/holes) play crucial roles. Previous studies have shown that constructing composite semiconducting materials is an effective way of achieving good separation of photoexcited charge carriers and subsequent redox reactions on the catalyst surface, thus improving the photocatalytic efficiency [11–15].

Based on the above considerations, we developed a novel graphene/tourmaline/TiO_2 (G/T/TiO_2) composite system. TiO_2 has been widely studied as a photocatalyst for water splitting and photodegradation of organic pollutants [1–4,16,17] because of its chemical inertness, cost effectiveness, environmental friendliness, and stability against light and chemical corrosion [18]. However, bare TiO_2 usually has the drawbacks of

* Corresponding author. Tel/Fax: +81-22-27405065; E-mail: defawang@tju.edu.cn
This work was supported by the National Basic Research Program of China (973 Program, 2014CB239300), the National Natural Science Foundation of China (51572191), and the Natural Science Foundation of Tianjin (13JCYBJC16600).
DOI: 10.1016/S1872-2067(17)62795-5| http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 8, August 2017

limited light-absorption ability (UV only) and rapid recombination of photoinduced charge carriers, leading to a poor photocatalytic performance when the entire solar spectrum is taken into account. Because of their intrinsic stoichiometry, graphene oxide (GO) exfoliated nanosheets are anionic two-dimensional materials with large surface areas [19,20]. This unique two-dimensional structure makes graphene an excellent catalyst support with good electronic conductivity/mobility. The use of semiconductor/graphene materials as photocatalysts with enhanced activities has been reported [21,22]. Graphene has also been used as an efficient cocatalyst with high activity in the photodegradation of organic pollutants [23] and photocatalytic hydrogen evolution [24]. Tourmaline is a borosilicate mineral with the R3*m* space group [25]. The general chemical formula of tourmaline is $XY_3Z_6Si_6O_{18}(BO_3)_3W_4$, where X is K^+, Na^+, Ca^{2+}, or a vacancy; Y is Mg^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, V^{3+}, or Ti^{4+}; Z is Al^{3+}, Fe^{3+}, Mg^{2+}, Cr^{3+}, V^{3+}, or Fe^{2+}; and W is OH^-, O^-, or F^-. Tourmaline has a single-symmetry polar axis and shows both pyroelectric and piezoelectric properties [26]. The electrostatic field on the surface of tourmaline arises from silicon-oxygen octahedral distortion [26,27] and its direction is parallel to the *c* axis, i.e., opposing charges are present at different ends of tourmaline particles. The electric field strength increases with decreasing tourmaline particle size. When the particles are micron sized, the tourmaline surface has an electric field of strength 10^6–10^7 V/m [25]. It is supposed that the electric field formed on the tourmaline surface plays an important role in the separation/transportation of photoexcited charge carriers, and therefore affects the photocatalytic activity of a composite semiconductor system containing tourmaline [28].

Here, we report the fabrication of G/T/TiO_2 composites using a two-step hydrothermal method. The mass percentage of each component in the composite was optimized based on the composite's performance in the photocatalytic degradation of 2-propanol (IPA). We found that the usually negatively charged surface of GO obtained by chemical delamination [20] could be modified to become positively charged [29,30]. We therefore investigated and compared the effects of the surface charged state of GO on the photocatalytic performances of the composites. We found that the electrostatic field on the tourmaline surface played an important role in the photocatalytic activity, and the activity of the composite with negatively charged GO was higher than that of the composite with positively charged GO. The related photophysical and photochemical mechanisms were also investigated. The results of our study provide an effective method for the development of composite photocatalytic systems in which the charge carrier separation, and therefore the photocatalytic properties, can be modified by tailoring the surface charged state (e.g., GO) and/or by introducing an external field (electric or magnetic) arising from a specific component (e.g., tourmaline) in the composite.

2. Experimental

2.1. Synthesis of GO

GO was prepared from natural graphite powder using a modified Hummers method. Typically, graphite powder (3.0 g) was dropped into a beaker of concentrated sulfuric acid (120 mL), which was cooled in an ice-water bath. Then potassium permanganate (15 g) was gradually added to the mixture. After stirring in the ice-water bath for 2 h, the mixture was transferred to water at 308 K and stirring was continued for 1 h. The temperature was raised to 338 K, water (250 mL) was added, and the mixture was stirred gently for 2 h. The mixture was diluted with water to 1400 mL, H_2O_2 aqueous solution (30 wt%, 30 mL) was added, and the reaction was continued for 20 min. The suspension was centrifuged and washed with aqueous hydrochloric acid solution (10 wt%) until no sulfate ion was detected. The obtained GO was freeze dried [31].

2.2. Synthesis of PDDA-Functionalized GO

GO was modified with poly(diallyldimethylammonium chloride) (PDDA; 20 wt% in water, M_w = (2–3) × 10^5) as follows. GO (100 mg) and water (100 mL) were placed in a 200 mL beaker and the mixture was ultrasonicated for 2 h until the dispersion became clear, without any visible particles. The PDDA (30 mg) solution was mixed with water (100 mL). The GO suspension was slowly added dropwise, at a rate of 2 μL/min, to the PDDA solution under stirring and the mixture was stirred overnight. Excess polymer was removed by repeated centrifugation (1 × 10^4 r/min, 10 min) with deionized (DI) water and the PDDA-modified GO (denoted by P-GO) was dried in a vacuum oven for 10 h [30].

2.3. Synthesis of G/T/TiO_2 Composites

The ternary composites were synthesized using a two-step hydrothermal method. Briefly, a mixture of GO (50 mg) or P-GO (50 mg) and tourmaline (schorl, 500 mg) was dispersed in water (26 mL). The dispersion was transferred to a 50 mL Teflon-lined stainless-steel autoclave; the autoclave was sealed tightly, and heated at 453 K for 10 h. After cooling naturally, the black-gray precipitates were collected by centrifugation, washed alternately with DI water and ethanol several times, and dried in a vacuum oven at 343 K for 4 h. The same method was used with different amounts of GO or P-GO (0, 0.1%, 0.5%, and 1% by mass) and different amounts of tourmaline (0, 1%, 5%, and 10% by mass) in the starting material solution. Graphene/tourmaline powders were obtained after washing and drying at 353 K for 10 h. The prepared graphene/tourmaline powders were mixed with tetrabutyl titanate (TBT; 1.28 mL) and dispersed in water (26 mL). The aqueous solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave and heated at 453 K for 10 h. Finally, the products were washed alternately with ID water and ethanol several times. The samples were denoted by G*X*/T*Y*/TiO_2 and P-G*X*/T*Y*/TiO_2, where *X* (0–1) and *Y* (0–10) are the mass percentages of graphene and tourmaline, respectively. For comparison, TiO_2 powders were also synthesized using the hydrothermal method under the same conditions but without adding GO and tourmaline.

2.4. Material Characterization