



Visible light-driven photocatalytic degradation of rhodamine B and industrial dyes (texbrite BAC-L and texbrite NFW-L) by ZnO-graphene-TiO₂ composite



Prawit Nuengmatcha^a, Saksit Chanthai^a, Ratana Mahachai^a, Won-Chun Oh^{b,*}

^a Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^b Department of Advanced Materials Science & Engineering, Hanseo University, Chungnam 356-706, South Korea

ARTICLE INFO

Article history:

Received 8 January 2016

Received in revised form 7 March 2016

Accepted 29 March 2016

Available online 29 March 2016

Keywords:

ZnO-graphene-TiO₂

Photocatalytic degradation

Rhodamine B

Catalyst

ABSTRACT

Visible light-responsive ZnO-graphene-TiO₂ (ZGT) composite catalyst was successfully synthesized via a simple solvothermal process. The intrinsic characteristics of as-obtained samples were examined using a variety of techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDS). The band gap energies of the samples were evaluated by UV–vis diffuse reflectance spectroscopy (UV–vis DRS). The photocatalytic activities of as-obtained catalysts were assessed based on the degradation of rhodamine B (RhB), texbrite BAC-L (TBAC) and texbrite NFW-L (TNFW) under visible-light irradiation. ZGT exhibited higher visible-light-activated photocatalytic activity than did other samples (ZGT ($7.97 \times 10^{-4} \text{ min}^{-1}$) > ZG ($3.43 \times 10^{-4} \text{ min}^{-1}$) > graphene ($2.43 \times 10^{-4} \text{ min}^{-1}$) > TiO₂ ($2.22 \times 10^{-4} \text{ min}^{-1}$) > ZnO ($1.87 \times 10^{-4} \text{ min}^{-1}$)). In addition, ZGT showed higher enhanced photocatalytic degradation of RhB than did other dyes (RhB ($7.97 \times 10^{-4} \text{ min}^{-1}$) > TNFW ($5.20 \times 10^{-4} \text{ min}^{-1}$) > TBAC ($2.48 \times 10^{-4} \text{ min}^{-1}$)). It is therefore evident that the synthesized ZGT can be used as a high performance catalyst for dye wastewaters. Moreover, the detailed photocatalytic mechanism of the photodegradation process is discussed.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Dyes and pigments are widely used in various industries to make precise colors in manufactured products and in biological laboratories for analytical purposes or as biological stains [1]. Rhodamine B (RhB) is a fresh peach-colored synthetic dye widely used as a colorant in the manufacturing of textiles, leathers, paints, and foods, and in laboratories [2]. The discharge of RhB into the aquatic environment results in wastewaters with high toxicity and low transparency. Moreover, it can irritate the eyes, skin, and respiratory system and it is carcinogenic and toxic to the reproductive and nervous systems [2]. Therefore, it is necessary to remove this contaminant from wastewater before releasing water into the environment to protect both the environment and human beings.

Several common wastewater treatment technologies for RhB dye have been studied, such as extraction [3], electrochemical oxidation [4], ion flotation [5], ion exchange membrane [6],

sonocatalytic degradation [7], advanced oxidation process [8], swirling jet-induced cavitation and hydrodynamic cavitation [9,10], membrane [11], adsorption [12–14] and photocatalytic degradation [15–17]. Of the above technologies, photocatalytic degradation is the most effective method of converting toxic organic contaminants into carbonaceous products [18]. Some other techniques merely transfer dye pollutants from one phase to another, and the pollutants are not well degraded or removed. Therefore, many scientists prefer the photocatalytic degradation process.

Various composite catalysts have been considered for photocatalytic degradation of rhodamine B dye, such as graphitic carbon nitride/reduced graphene oxide (g-C₃N₄/rGO) [19], SnO₂/ZnS [20], Y₂InSbO₇ and Y₂GdSbO₇ [21], CoFe/SBA-15 catalyst coupled with peroxy-monosulfate [22], WO₃ [23], PPy/Bi₂O₂CO₃ [24], HgI₂ [25], PbS/QDs-Bi₂WO₆ [26], Ag@AgBr-intercalated K₄Nb₆O₁₇ composite [27], ZnFe₂O₄ [28], La₂O₃/Ag₃VO₄ [29], pure bismuth ferrite (BiFeO₃) [30], Fe₂O₃-Kaolin [31], g-C₃N₄/SiO₂-HNb₃O₈ [32], Fe₃O₄@SiO₂@ZnO-Ag core-shell microspheres [33], Ag₃PO₄ dispersed on exfoliated bentonite (EB-Ag₃PO₄) [34], and Ag@AgBr/SBA-15 [35]. However, because these composite materials have some drawbacks such as the need for UV activation and complex

* Corresponding author.

E-mail address: wc_oh@hanseo.ac.kr (W.-C. Oh).

preparation procedures, new composite catalysts have recently been developed.

In recent years, both TiO_2 and ZnO have been shown to be promising catalyst materials and have been widely applied for photocatalytic degradation of dye pollutants due to their low cost, chemical inertness, non-toxicity, ready availability, complete mineralization, and stability. However, both catalysts have some drawbacks. TiO_2 requires an excitation wavelength that falls in the UV region of 300–390 nm [36], and also exhibits a high rate of electron-hole recombination [37]. Therefore, it is not suitable for the removal of non- or low-transparency dye wastewaters. The photocatalytic performance of ZnO is limited because of both its fast charge carrier recombination and its low interfacial charge transfer rate [38]. Hence, the development of well-defined TiO_2 and ZnO -based photocatalysts with narrow band gap energies, excellent visible light absorption capabilities, and highly efficient dye degradation capacities is an active area of interest.

To enhance the photocatalytic activity of both TiO_2 and ZnO , many studies have been conducted on the addition of small amounts of different compounds such as iron [39], nitrogen and fluoride [40], carbon and sulfide [41], etc., to the semiconductor. The inclusion of such dopants can change the distribution of electrons in the system and affect the surface properties of the semiconductor photocatalyst, thereby improving photocatalytic performance [33]. In addition, a novel way to improve photocatalytic efficiency is the introduction of carbon materials, especially graphene. Recently, graphene has been shown to be one of the best catalysts for the photocatalytic degradation process; it achieves effective degradation as it both scavenges and shuttles electrons simultaneously, therefore minimizing recombination issues.

Our research group recently reported a simple strategy for the fabrication of oxygen-rich metal oxide and TiO_2 photocatalysts with enhanced visible light photoactivity [37]. By simply modifying the titanium precursor, the band gap-engineered ternary ZnO-G-TiO_2 displayed high photocatalytic performance towards non-degradable organic dyes under visible light irradiation. Even so, the photoactivity of bare TiO_2 was found to gradually deteriorate over time. This could be due to the rapid recombination of photoinduced charge carriers. Hence, the present work focuses on improving photoactivity and stability of ZnO-G-TiO_2 by further promoting the visible light response and suppressing the charge

recombination rate through the use of a cost-effective support nanostructure. While there have been numerous papers reporting the fabrication of graphene- TiO_2 composites, there is no prior study on the synthesis of a ZnO-G-TiO_2 photocatalyst and its performance in the reduction of non-degradable commercial dyes under visible light irradiation. Hence, in the present work, we relate for the first time a proof-of-concept study on the enhancement of photocatalytic activity via a combined strategy of fabricating visible-light responsive ternary heterostructure and improving overall photostability by incorporating GO sheets.

2. Materials and methods

2.1. Materials

Titanium (IV) *n*-butoxide (TNB, $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) as a Ti source for both TiO_2 and the ZGT composite preparation was purchased from Kanto Chemical Company (TOKYO, Japan). Hydrogen peroxide 30% (H_2O_2), Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and sulfuric acid (H_2SO_4) were purchased from Daejung Chemicals & Metals Co., Ltd, Korea. Methanol (CH_3OH) was purchased from Merck, Germany. Rhodamine B (RhB, $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$), two types of industrial dye (Texbrite BAC-L and Texbrite NFW-L), which were used as model dye pollutants were purchased from Samchun Pure Chemical Co., Ltd., Korea and potassium permanganate (KMnO_4) was purchased from Texchem Co., Ltd., Korea. All chemicals were used without further purification in all experiments.

2.2. Preparation of composite catalysts

Graphene oxide was prepared from graphite by the modified Hummers' method. In brief, 20 g of graphite and concentrated H_2SO_4 (460 ml) were mixed in a beaker at 0°C with vigorous magnetic stirring. Next, 60 g of KMnO_4 was slowly added to the beaker and the mixture was kept below 15°C . The mixture was stirred at 35°C until its colour changed to brown, and then the mixture was diluted with 750 ml deionized (DI) water and kept below 90°C with stirring. After that, the beaker was sealed and kept at 100°C with vigorous stirring for 30 min, and 20% H_2O_2 was slowly added. Then, the mixture was washed with water, acetone, and 10% HCl solution in that order to eliminate residual metal ions, and the sample was heated in a dry oven at 90°C for 12 h to give graphite oxide powder. For graphene oxide preparation, 300 mg of graphite oxide powder and 250 ml DI water were mixed in a beaker, stirred, and ultrasonicated for 30 and 120 min. The mixture was filtered and washed with hot water and heated in a dry oven for 12 h to yield graphene oxide (GO) powder.

For ZGT preparation, 300 mg GO , 70 mg $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 250 mL H_2O were mixed in a beaker. Then, the mixture was ultrasonicated for 2 h and stirred for 5 h at 90°C . After removal of the solvent at 100°C , the solid samples were heat-treated in a furnace at 600°C for 2 h to give ZnO-graphene (ZG) (solution A). Furthermore, to obtain a colloidal TiO_2 solution, 2 mL TNB and 250 mL CH_3OH were mixed and sonicated for 2 h (solution B). After that, 50 mg A was added to solution B and heated to 60°C for 5 h. To remove the solvent, the mixture was heated to 80°C . The obtained solid was heat-treated in a furnace at 600°C for 2 h to yield ZGT. For comparison, all samples including ZnO , TiO_2 , and graphene were prepared using a similar process with slight modifications.

2.3. Characterization of catalysts

The XRD patterns of the prepared samples were taken using an X-Ray diffraction spectrometer (Shimada XD-D1, Japan) with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) at a scan speed of 1.2° m^{-1} . The surface morphologies of all samples were taken with scanning electron

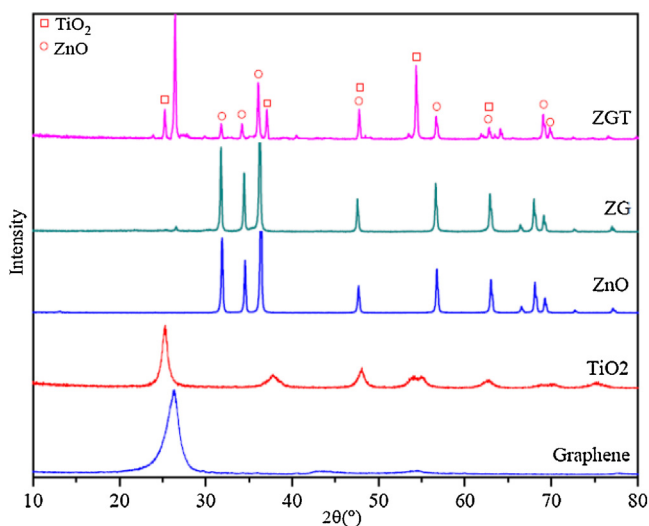


Fig. 1. XRD patterns of graphene, TiO_2 , ZnO , ZG and ZGT.

Download English Version:

<https://daneshyari.com/en/article/221701>

Download Persian Version:

<https://daneshyari.com/article/221701>

[Daneshyari.com](https://daneshyari.com)