Journal of Photochemistry & Photobiology A: Chemistry 368 (2019) 110–119

Contents lists available at ScienceDirect

Journal of Photochemistry & Photobiology A: Chemistry

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

Facile synthesis of porous metal-doped ZnO/g-C_3N_4 composites for highly efficient photocatalysts

Qui Thanh Hoai Ta, Gitae Namgung, Jin-Seo Noh*

Department of Nano-Physics, Gachon University, 1342 Seongnamdaero, Sujeong-gu, Seongnam-si, Gyeonggi-do, 13120, Republic of Korea

ARTICLE INFO

Keywords:
Mg-doped ZnO/g-C_3N_4 composite
One-pot pyrolysis
Porous structure
Photocatalytic activity
Methylene blue

ABSTRACT

Metal (M)-doped ZnO/g-C_3N_4 composites with a sponge-like porous structure have been synthesized by a facile one-pot pyrolysis method. A representative composite, magnesium (Mg)-doped ZnO/g-C_3N_4 composite was analyzed to contain a 13.7 at% of ZnO and Mg at a standard condition. ZnO and Mg were uniformly distributed over the composite without the formation of clearly separated phases. Optical properties of the composite revealed the extension of light absorption range and the suppressed carrier recombination. Most notably, the photocatalytic efficiency of the Mg-doped ZnO/g-C_3N_4 composite overwhelmed those of pure ZnO, pure g-C_3N_4, ZnO/g-C_3N_4 composite, and ZnO/g-C_3N_4 composites doped with other metals. Its photoreaction rate constant was estimated to be even higher than the previous reports. A physical mechanism was proposed to account for the observed enhancement of the photocatalytic activity. The synthetic approach and the demonstrated performance of this work may present new direction towards high-performance photocatalysts using composites of g-C_3N_4 and ZnO.

1. Introduction

Discharge of waste matters from industry and home has been an ever-increasing hazard to the environment. Photocatalysis is an eco-friendly technology to tackle the serious issue, in which a light-activated catalyst degrades organic pollutants in waste water or contaminated air [1–4]. Inorganic semiconductors such as zinc oxide (ZnO) [5,6], titanium oxide (TiO_2) [7,8], and tin oxide (SnO_2) [9,10] have been widely explored as photocatalysts. Of them, ZnO attracted most interest due to its non-toxicity, low cost, and high quantum efficiency [5,11]. However, the band gap (E_g = 3.37 eV) of ZnO is too wide to absorb the visible light, which accounts for 46% of solar spectrum [6,12]. A variety of methods have been proposed to shift the light absorption edge of ZnO to longer wavelengths, including doping with impurity ions, surface sensitization with dyes, and coupling with other semiconductors [13–15]. Doping ZnO with impurities has been proved to be effective in the absorption edge shift, as typified by Na-doped ZnO [16] or by Sb-doped ZnO [17]. However, the search for an optimal dopant needs to be continued because the photocatalytic efficiency of doped ZnO is not good enough under visible light.

Graphitic carbon nitride (g-C_3N_4) is a metal-free semiconducting polymer with unique 2D stacked structure similar to that of graphite [18]. Its narrower band gap (E_g = 2.7 eV) allows for catalytic applications working in the visible light range [19,20]. Chemical and thermal stability, non-toxicity, and ease of synthesis are another advantages of g-C_3N_4 [20–22]. Owing to these advantages, many efforts have recently been made to employ this material for hydrogen generation by water splitting, reduction of carbon dioxide, and degradation of organic pollutants [20,23]. However, the practical applications of g-C_3N_4 were restricted mainly due to the high recombination rate of photogenerated charge carriers [21,24]. Similar to ZnO, several approaches have been taken to improve the photocatalytic activity of g-C_3N_4, including incorporation of dopants and coupling with other semiconductors. For instance, TiO_2/g-C_3N_4 heterojunction anode [25], 2D/2D g-C_3N_4/MnO_2 nanocomposites [26], g-C_3N_4-RGO-TiO_2 composites [27], WO_3/g-C_3N_4/Ni(OH)$_x$ hybrids [28], $ZnMoO_4$/g-C_3N_4 composites [29], and g-C_3N_4/porous silicon (pSi) composites all showed improved photocatalytic performance compared to pure g-C_3N_4 [30]. Furthermore, ZnO/g-C_3N_4 composites, which may be a material combination with particular importance, have also demonstrated the enhancement of visible-light-driven photocatalytic efficiency [31–33]. Although the hybridization of ZnO and g-C_3N_4 achieved synergistic effects to overcome major shortcomings of the respective materials, the effect of metal doping on the photocatalytic activity of ZnO/g-C_3N_4 composites has not been addressed.

In this work, porous, metal (M)-doped ZnO/g-C_3N_4 composites were

* Corresponding author.
E-mail address: jinseonoh@gachon.ac.kr (J.-S. Noh).

https://doi.org/10.1016/j.jphotochem.2018.09.049
Received 6 August 2018; Received in revised form 11 September 2018; Accepted 26 September 2018
Available online 28 September 2018

Table 1
Synthesis conditions of pure ZnO, Mg-doped ZnO, pure C_3N_4, ZnO/g-C_3N_4 composite, and various M-doped ZnO/g-C_3N_4 composites.

Sample	$Zn(NO_3)_2$ (M)	$Mg(NO_3)_2$ (M)	CH_4N_2O (g)	Temperature (°C)	Reaction time (h)
ZnO	0.2	0	0	550	2
Mg-ZnO	0.2	0.2	0	550	2
g-C_3N_4	0	0	10	550	2
ZnO/g-C_3N_4	0.2	0	10	550	2
Mg-ZnO/g-C_3N_4	0.2	0.2	10	550	2
Al-ZnO/g-C_3N_4	0.2	0.2	10	550	2
Mn-ZnO/g-C_3N_4	0.2	0.2	10	550	2
4Mg-ZnO/g-C_3N_4	0.8	0.2	10	550	2
Mg-0.5ZnO/g-C_3N_4	0.2	0.1	10	550	2

synthesized using a facile one-pot pyrolysis method, in which three kinds of metal precursors were employed for doping. The composites were characterized by unique sponge-like morphologies and even distributions of ZnO and metal dopants. It was demonstrated that the photocatalytic efficiency of magnesium (Mg)-doped ZnO/g-C_3N_4 composites was significantly enhanced from those of pure g-C_3N_4 and ZnO/g-C_3N_4 composites.

2. Experimental

2.1. Materials

Urea (CH_4N_2O) and zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) were used as precursors of g-C_3N_4 and ZnO, respectively. Magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$), manganese (II) nitrate tetrahydrate ($Mn(NO_3)_2{\cdot}4H_2O$), and aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$) were introduced for doping. All of these precursors were purchased from Sigma-Aldrich, and they were used without further purification. Methylene blue (MB) was used as probe dye for the photocatalytic activity of individual photocatalysts.

2.2. Synthesis of M-doped ZnO/g-C_3N_4 composites

M-doped ZnO/g-C_3N_4 composites were easily synthesized by an one-pot pyrolysis method, in which precursors of all constituents were mixed into a solution, then it was heat-treated together. At a standard condition, a 0.594 g (0.2 M) of $Zn(NO_3)_2{\cdot}6H_2O$ and a 0.2 M of metal precursor were dissolved and stirred in 10 ml of deionized (DI) water at room temperature, which produced a salt solution including both Zn^{2+} and metal ions. Then, a 10 g of CH_4N_2O was added to this precursor solution. At the next step, the solution was placed in the oven at 60 °C to remove DI water, resulting in a powder. The powder was then transferred into an alumina crucible with a cover and it was heated in a muffle furnace at 550 °C for 2 h. Finally, the ash powders were collected from the crucible after natural cool-down to room temperature. Furthermore, pure ZnO, pure g-C_3N_4, and undoped ZnO/g-C_3N_4 composite were independently synthesized at standard conditions for comparison. In addition, Mg-doped ZnO and Mg-doped ZnO/g-C_3N_4 composites with different compositions were also prepared to see the composition-dependent effects. The details of synthesis conditions are summarized in Table 1.

2.3. Material characterization

Nanoscale and microscale morphologies of various M-doped ZnO/g-C_3N_4 composites were analyzed using a field emission scanning electron microscope (FE-SEM, JEOL JSM-7500 F) and a transmission electron microscope (TEM, Technai G2 F30 S-Twin). In particular, the morphology and element distributions of Mg-doped ZnO/g-C_3N_4 composite were further examined utilizing another FE-SEM (Hitachi S-4700) mounted with an energy-dispersive X-ray (EDX) spectrometer. Crystalline features of ZnO, g-C_3N_4, and M-doped ZnO/g-C_3N_4 composite were characterized by X-ray diffraction (XRD, X'Pert Pro MPD), while X-ray photoelectron spectroscopy (XPS, K-Alpha-Thermo electron) was utilized for the composition analysis. To study the effect of sample composition and synthesis condition on optical properties, UV–vis diffuse reflectance spectra (UV–vis DRS) and photoluminescence (PL) spectra were measured using a Cary 5000 spectrophotometer and a Cary Eclipse fluorescence spectrophotometer, respectively. Thermal characteristics of ZnO, g-C_3N_4, and M-doped ZnO/g-C_3N_4 were also examined by thermo gravimetric analysis (TGA, SDT Q600 V20.9) with a heating rate of 10 °C min^{-1} under N_2 flow (100 mL min^{-1}). Furthermore, the Brunauer-Emmett-Teller (BET) surface areas were estimated for selected samples using a surface area and porosimetry system (ASAP 2020 V3.04 H). Powder samples were used for the above material characterizations except for PL measurement, where a 0.01 mg of sample was dissolved in 5 ml of DI water and sonicated for 15 min.

2.4. Photocatalytic tests

The photocatalytic activity of M-doped ZnO/g-C_3N_4 composites was evaluated by the degradation of MB solution under light that was illuminated from a solar simulator. The photocatalytic performance of pure ZnO, pure g-C_3N_4, and Mg-doped ZnO was also examined at the same illumination conditions. For these photocatalysis tests, a 20 mg of catalyst was dispersed in 50 ml of MB solution (5 mg L^{-1}) and stirred for 5 min. For time-dependent visual inspection and UV–vis analysis, 5 ml of samples were sequentially taken out of the solution at a 20 min time interval (20, 40, 60 min). After each test, the photocatalyst was separated from the solution by centrifugation for recycling.

3. Results and discussion

3.1. Morphologies

Fig.1 shows SEM images of pure ZnO, pure g-C_3N_4, undoped ZnO/g-C_3N_4 composite, and Mg-doped ZnO/g-C_3N_4 composite. All samples were prepared by the same pyrolysis conditions (550 °C, 2 h). ZnO resembles microflowers with polypyramid-shaped stamens and faceted petals, which are somewhat different from typical ZnO morphologies (Fig. 1a). On the other hand, g-C_3N_4 holds crumpled sheet structures (Fig. 1b) that have been often observed for g-C_3N_4 pyrolyzed from urea [34,35]. Interestingly, the morphologies of ZnO/g-C_3N_4 composite and Mg-doped ZnO/g-C_3N_4 composite are distinct from those of ZnO and g-C_3N_4 (see Fig.1c – f). They show irregularly distributed sponge-like structures with many small pores. In terms of the morphology, the two kinds of composites are too similar to distinguish from each other. For both undoped and Mg-doped ZnO/g-C_3N_4 composites, it is difficult to perceive the spatial distributions of ZnO and g-C_3N_4 components separately. The characteristic shapes of the respective components are unobvious. Irregular, porous structures similar to that of Mg-doped ZnO/g-C_3N_4 composite are also found in Mn-doped and Al-doped ZnO/g-C_3N_4 composites, as shown in Fig. S1. A minor difference is that Mg-doped ZnO/g-C_3N_4 composite has more sponge body compared to the other M-doped ZnO/g-C_3N_4 composites, where many crumpled particles appear.

Fig.2 displays low and high-resolution TEM images of Mg-doped ZnO/g-C_3N_4 composite. As can be seen in Fig. 2b, the composite consists of randomly distributed tiny crystallites (marked with dotted lines) and amorphous matter between them. The interlayer spacing of the crystallites is measured at 0.32 nm, which is close to the *d* spacing of (002) plane of g-C_3N_4, signifying that the crystallites were originated