



# Photocatalytic synthesis of reduced graphene oxide–zinc oxide: Effects of light intensity and exposure time



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## ARTICLE INFO

### Article history:

Received 5 January 2017

Received in revised form 18 February 2017

Accepted 12 March 2017

Available online 18 March 2017

### Keywords:

rGO–ZnO

Photocatalytic reduction

Light intensity

Exposure time

Defect

Charge transfer

## ABSTRACT

A series of composites containing reduced graphene oxide and zinc oxide (rGO–ZnO) with optimum GO loading amount of 3 wt% was successfully synthesized through an *in-situ* photocatalytic reduction of graphene oxide (GO) over ZnO photocatalyst under UV light irradiation. Different light intensities and exposure times were confirmed to affect the properties and photocatalytic performance of the rGO–ZnO for photocatalytic degradation of phenol as an organic pollutant model. The best photocatalyst was obtained under UV light intensity of  $0.4 \text{ mW cm}^{-2}$  for 24 h exposure and it gave around three times higher photocatalytic performance than that of the bare ZnO. Compensating for the long exposure time, such low light intensity was crucial to generate rGO with low amount of defects. The low amount of defects resulted in low electron-hole recombination, low resistance of a charge transfer, and high electron-transfer rate constant, which in turn enhanced the photocatalytic performance. Reusability tests demonstrated the potential use of rGO–ZnO as a good photocatalyst for organic pollutant degradations.

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## 1. Introduction

Owing to the issues on the water treatment and energy sustainability, exploration on the highly efficient photocatalysts for treating wastewater containing harmful organic pollutants is immensely reported worldwide. In recent decades, zinc oxide (ZnO) has been an attractive photocatalyst [1–10] due to its excellent and remarkable physicochemical properties, including wide band gap (3.37 eV), chemical inertness, and strong oxidation ability. While the photocorrosion under solar light can be neglected [1], ZnO suffered from photocorrosion when illuminated under UV light irradiation [2–7,11], and it has a high rate of charge recombination, which practically hindered its applications for numerous types of reactions. In order to suppress the drawbacks of ZnO, many attempts were made to increase the performance of ZnO by modifications with dopants, carbon materials, semiconductor coupling, and dye sensitization [2,11–17].

One of the recent promising modifiers is graphene-based materials. This two-dimensional (2D) material has been put to use especially as the modifier for photocatalysts, owing to its exceptionally unique characters, such as high electron conductivity, excellent mechanical properties, large specific surface area and high thermal stability [18–23]. Despite of the exceptional properties of graphene (GR), graphene oxide (GO) is more favourable as the modifier since oxygen functional groups are important to produce stronger interaction in the hybrid composite photocatalysts [24,25]. However, as GO itself is an insulator, in order to restore the electron conductivity of GO sheets, it is usually partially reduced to reduced graphene oxide (rGO).

The rGO–ZnO composite has been commonly synthesized by several strategies, such as microwave-assisted reaction, hydrothermal, solvothermal, hydrolysis methods, thermal expansion of GO under inert atmosphere by nitrogen, surface coating and liquid arc discharge [26–32]. Unfortunately, the implementation of heat treatment is less favourable since it forms rGO with less crystalline structure and more defects. Thermal expansion of GO under nitrogen and hydrogen atmospheres at lower temperature might overcome the less crystalline of formed rGO. However, it causes a complete reduction of oxygen functionalities on the GO structure, which is less desired since oxygen functionalities are crucial to

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provide interactions with ZnO. Moreover, the reduction of GO to rGO by using toxic reducing agents such as hydrazine ( $\text{N}_2\text{H}_4$ ) introduced residue of reductant into the rGO suspension. On the other hand, liquid arc discharge method can successfully create high quality of rGO, but further purification is needed to remove the unwanted carbon. Therefore, an alternative strategy using UV light to assist the reduction process in the presence of suitable photocatalyst should be adopted.

Williams *et al.* first demonstrated a clean and environmental-friendly reduction method to convert GO to rGO using ZnO as photocatalyst under UV light irradiation at room temperature [33]. This approach has some valuable advantages. For examples, this method did not use toxic reducing agents, did not produce any impurities and produce partially reduced oxygen functionalities on rGO structure which are useful on providing interactions between rGO and ZnO. This method also offered mild conditions for the synthesis process. The photocatalytic property of the rGO-ZnO prepared by this mild method was first reported for reduction of Cr (VI) [34]. It was obtained that the rGO-ZnO composite gave 1.5 times higher photocatalytic activity than that of the bare ZnO since the electron-hole recombination on ZnO was successfully suppressed and the light absorption capability was improved in the presence of the rGO.

Herein, we reported the effects of light intensity and exposure time on the properties and performance of rGO-ZnO composites prepared by the reduction method carried out photocatalytically over the ZnO as the photocatalyst. Light intensity and exposure time are considered to be crucial to prepare the rGO-ZnO composites, which however, have never been addressed yet. The use of strong light intensity might lead to the extensive reduction or destruction of GO. On the other hand, the duration of the synthesis time shall be also optimized for efficiency and avoiding the over-reduction of the GO. Notably, we could obtain the rGO-ZnO with much better photocatalytic performance (3.4 times) as compared to the bare ZnO when it was synthesized using low UV light intensity ( $0.4 \text{ mW cm}^{-2}$ ) and enough irradiation time (24 h). The superior photocatalytic performance of the composite was strongly related to formation of defects in low amount that promoted charge separation and improved electron charge transfer between the rGO and the ZnO, as evidenced by Raman, electrochemical impedance spectroscopies (EIS), and photocurrent investigations.

## 2. Experimental

### 2.1. Synthesis of ZnO

ZnO was synthesized by a simple co-precipitation method according to the reported literature [3] using zinc acetate dehydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , 99.5%, QRèc) as the starting precursor. Briefly, the  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (4.5 g) was dissolved in deionized water (100 mL) and then sonicated for 30 min to obtain solution A. In order to prepare solution B, sodium hydroxide (NaOH, 99%, QRèc, 6.4 g) was dissolved in deionized water (100 mL) and hexadecyltrimethylammonium bromide ( $((\text{C}_{16}\text{H}_{33})\text{N}(\text{CH}_3)_3\text{Br}$ , 99%, Merck, 7.28 g) was added into the solution, followed by stirring for 1 h to make the solution homogeneous. Subsequently, the solution A was added slowly into the solution B and then heated at  $70^\circ\text{C}$  for 1 h. The remaining solid was filtered and washed by deionized water and ethanol, consecutively. The as-prepared ZnO was dried and calcined at  $500^\circ\text{C}$  in air with a ramp rate of  $1.0^\circ\text{C min}^{-1}$  and further tempered for another 1 h at this temperature. The resulting white solid was subsequently ground to get the ZnO powder.

### 2.2. Synthesis of GO

The improved Hummers' method was adopted to synthesize GO [35]. Graphite flakes (C, 99%, Merck, 1 g) and potassium permanganate ( $\text{KMnO}_4$ , 99.5%, 6 g) were added into a 500 mL of round bottom flask, followed by addition of concentrated sulphuric acid ( $\text{H}_2\text{SO}_4$ , >95%, Fisher Scientific, 135 mL) and phosphoric acid ( $\text{H}_3\text{PO}_4$ , 85%, Merck, 15 mL) with ratio of 9:1. The mixture was stirred at  $50^\circ\text{C}$  for 24 h. Upon completion of reaction and cooling to room temperature, it was poured into ice water (400 mL). The solution was quenched with the addition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%, Fisher Scientific, 5 mL) in order to reduce permanganate that might be remained. The solid was later collected by centrifuging the mixture for about 10 min (4000 rpm). The solid obtained was further washed two times with hydrochloric acid (HCl, 30%, Fisher Scientific, 200 mL) and distilled water by centrifugation until pH solution was near to 7, consecutively. Upon reaching pH of 7, the solid was dispersed into methanol ( $\text{CH}_3\text{OH}$ , 99.99%, Fisher Scientific, 100 mL), followed by sonication for 1 h. The solution was then evaporated at  $40^\circ\text{C}$  and vacuum dried overnight at room temperature.

### 2.3. Synthesis of rGO-ZnO

rGO-ZnO composites were prepared through a photocatalytic reduction method using ZnO as the photocatalyst to reduce GO [34] using different weight ratios of GO, light intensities and duration times. The weight ratios of GO were fixed at 0.5, 1, 3, 5, and 10 wt%. As a typical synthesis of 3 wt% rGO-ZnO, the ZnO (1 g) was dispersed in methanol ( $\text{CH}_3\text{OH}$ , 99.99%, Fisher Scientific, 60 mL) and the prepared GO (0.03 g) was added to the mixture, followed by ultrasonication for 30 min. After sonication, the mixture was then exposed under UV light irradiation with a specific condition. The mixture was then filtered and subsequently washed by double distilled water and ethanol. The obtained solid was further dried at  $60^\circ\text{C}$  in an oven overnight. The 3 wt% rGO-ZnO sample was labelled as rGO(a,b)-ZnO, where a showed the light intensity of UV light with a varying from  $0.2$  to  $13.0 \text{ mW cm}^{-2}$ , while b represented the time exposure during photocatalytic reduction with b varying from 3 to 24 h.

### 2.4. Characterizations

The crystal structure of the synthesized rGO-ZnO composites was analysed by an X-ray diffractometer (XRD) using a Bruker Advance D8 diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at a scan rate of  $0.05^\circ \text{ s}^{-1}$ . The applied current and accelerating voltage used were 40 mA and 40 kV, respectively. The Fourier transform infrared (FTIR) spectra of the prepared composites were recorded by a Thermo Scientific Nicolet iS50 using pellet technique with potassium bromide (KBr). The stability of prepared sample and weight content analysis of rGO was analysed with a thermogravimetric analyzer (TGA) using a Mettler TGA/SDTA 851<sup>e</sup>. The samples were heated from  $50$  to  $800^\circ\text{C}$  with a heating rate of  $10^\circ\text{C min}^{-1}$ . In order to study the morphology of the samples, transmission electron microscope (TEM) images were recorded on a JEOL JEM-2100, which an accelerating voltage was set to 200 kV. The diffuse reflectance ultraviolet-visible (DR UV-vis) spectra were investigated by a Shimadzu UV-2600. Barium sulphate ( $\text{BaSO}_4$ ) was used as the reflectance standard. The fluorescence spectra of samples were measured at room temperature on a fluorescence spectrophotometer (JASCO, FP-8500). Both of excitation and emission bandwidths were fixed at 5 nm. Raman spectra of the prepared samples were measured by an XploRA Plus Raman Microscope HORIBA with the selected laser wavelength of 532 nm.

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