

## Facile in-situ formation of rGO/ZnO nanocomposite: Photocatalytic remediation of organic pollutants under solar illumination



Arunkumar Shanmugasundaram<sup>a,b,1</sup>, Ramireddy Boppella<sup>d,1</sup>, Yun-Jin Jeong<sup>a,b</sup>, Jongsung Park<sup>a,b</sup>, Young-Bae Kim<sup>b</sup>, Byungchul Choi<sup>b</sup>, Su Han Park<sup>b</sup>, Seunghun Jung<sup>b</sup>, Dong-Weon Lee<sup>a,b,c,\*</sup>

<sup>a</sup> MEMS and Nanotechnology Laboratory, School of Mechanical System Engineering, Chonnam National University, Gwangju, 61186, Republic of Korea

<sup>b</sup> School of Mechanical System Engineering, Chonnam National University, Gwangju, 61186, Republic of Korea

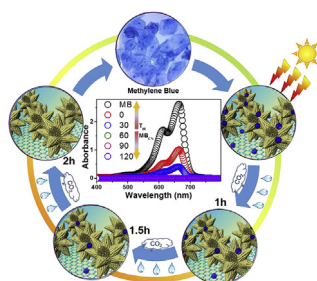
<sup>c</sup> Center for Next-generation Sensor Research and Development, Chonnam National University, Gwangju, 61186, Republic of Korea

<sup>d</sup> Nanomaterials Laboratory, Inorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Hyderabad, 500007, Telangana, India

### HIGHLIGHTS

- A new one-step approach yields ZnO/rGO hybrids with *in-situ* formation of heterojunctions.
- Ethanolamine used to mineralize the ZnO precursor and also facilitates the reduction GO *in-situ*.
- The ZnO/rGO heterojunctions show improved photo catalytic activity under solar light illumination.
- Plausible photo catalysis mechanism has been proposed.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

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### ABSTRACT

Herein, we present a facile hydrothermal route for the preparation of hierarchical mesoporous zinc oxide (ZnO) and reduced graphene oxide-zinc oxide ( $ZnO_{rGO}$ ) composites for degradation of organic pollutants from natural water resources. Morphologies of the as-synthesized materials were carried out by electron microscopy in scanning and transmission modes. Thermal stability of the as-prepared products was characterised by thermogravimetric-differential thermal analysis. Crystal structure and phase purity of the materials was characterised by powder x-ray diffraction, micro-Raman, and X-ray photoelectron spectroscopy analysis. Optical properties of the as-prepared materials were investigated by ultra violet-diffused reflectance and photoluminescence spectroscopy analysis. Photocatalytic activity of the as-prepared materials was estimated by evaluating the degradation kinetics of methylene blue (MB) dye in aqueous solution under standard solar light illumination. The calculated rate constant of the  $Zn_{rGO}$  is found to be  $\sim 2.831 \text{ h}^{-1}$  which is  $\sim 6.3$  times higher than the estimated rate constant of the as-prepared pristine ZnO ( $0.455 \text{ h}^{-1}$ ). The exceptional photocatalytic activity of the as-prepared  $Zn_{rGO}$  composites is attributed to the account of their synergetic effect, porous structure, and effective separation of charge carriers. Finally, based on the obtained experimental results viable photocatalytic mechanism has been proposed.

\* Corresponding author. MEMS and Nanotechnology Laboratory, School of Mechanical System Engineering, Chonnam National University, Gwangju, 61186, Republic of Korea.

E-mail address: [mems@jnu.ac.kr](mailto:mems@jnu.ac.kr) (D.-W. Lee).

<sup>1</sup> Authors are equally contributed.

## 1. Introduction

Increasing worldwide contamination of water resources has become one of the major environmental problems facing humanity [1]. Of all water impurities, organic dyes are one of the most important pollutants initiating a discrepancy to the environment, as it gets stored and moved through various organisms and/or along the food chain [2]. Therefore, removal of such toxic pollutants from water sources remains a major challenge that needs to urgently address. Over the years several techniques have been proposed to reduce the pollution growth such as adsorption, precipitation, reverse osmosis, just transfer the pollutants from toxic phase to another non-toxic phase and photocatalysis [3–5].

To date, photocatalysis based on metal oxide semiconductors such as  $\text{TiO}_2$ , ZnO, NiO,  $\text{In}_2\text{O}_3$ ,  $\alpha\text{-Fe}_2\text{O}_3$ , etc. have become a promising strategy for the degradation of organic pollutants [6–10]. In general, photocatalysis reactions are usually instigated through light energy, which is higher than the energy gap ( $E_g > h\nu$ ) of the photocatalyst [11]. The incident photon generates e-h (electron-hole) pairs on the surface of the photocatalyst, which is transforming noxious organic impurities into nontoxic by-products through chemical reduction-oxidation kinetics process. The final outcome of the photocatalysis reaction is generally  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Among extensive photocatalytically active materials, ZnO is an imperative wide direct bandgap semiconductor ( $E_g \sim 3.37$  eV) with large exciton binding energy (60 meV) at room temperature and usually exhibits a hexagonal wurtzite crystal structure [12]. ZnO has received significant attention in various fields of science & technology particularly as a photocatalyst, owing to its fascinating characteristics such as optical transparency, nontoxicity, electrochemical activity and biocompatibility [13,14]. However, proficiency of ZnO photocatalyst has met limited success because of its high recombination rate of e-h pairs, high photo-corrosion, and large bandgap ( $E_g > 3$  eV) which can absorb less than 5% of total solar light [15].

At present, several research efforts have been devoted to improve the efficiency of ZnO employing various approaches such as, doping, alloying with metallic elements such as gold [16], silver [17], platinum [18], nickel [19], vanadium [20], incorporation non-metal species like nitrogen [21], fluorine [22], sulphur [23] and addition of narrow bandgap semiconducting materials like Si [24],  $\text{In}_2\text{S}_3$  [25], CdSe [26]. For example, Zou et al. prepared heterogeneous lollipop-like  $\text{V}_2\text{O}_5/\text{ZnO}$  array and established their utility as a promising visible light photocatalytic material by decomposing 2,6-dichlorophenol (2,6-DCP) [27]. Sunita et al. successfully demonstrated the bandgap engineering of ZnO through  $\text{Ag}_2\text{S}$  sensitizer and the resultant material showed enhanced photocatalytic degradation in comparison to pristine ZnO [28].

Recently, the incorporation of carbon composites like carbon nanotube [29], graphene [30] is considered an effective method to improve the photocatalytic efficiency and to address the photo-corrosion of the photocatalyst [31]. rGO has been incorporated into several metal oxides and the resultant composites were successfully demonstrated as an effective photocatalyst, because of its improved charge transfer at the interface between the metal oxide and rGO, high surface area, and good adsorption capability [32]. For instance, Luo et al. prepared rGO incorporated hierarchical ZnO hollow sphere for degradation of methylene blue. The ZnO/rGO composites showed  $\sim 67\%$  enhanced photo-degradation efficiency compared to pristine ZnO hollow spheres [33].

In continuation of those great efforts, herein, we report a facile hydrothermal route for the preparation of hierarchical mesoporous ZnO nanoflower like architecture and  $\text{ZnO}_{\text{rGO}}$  composites for photocatalytic degradation of methylene blue (MB) dye. Firstly, graphene oxide (GO) was prepared by modified Hummer's method. The  $\text{ZnO}_{\text{rGO}}$  composites were prepared under hydrothermal condition by using zinc acetate dihydrate as the metal precursor, ethanolamine as an organic Lewis base, and water as the reaction medium. The ethanolamine was used to mineralize the ZnO from water-soluble zinc acetate dihydrate at the

same time it also facilitates the reduction of graphene oxide and their assembly to generate  $\text{ZnO}_{\text{rGO}}$  composites *in-situ*. To optimize the photocatalysis characteristics different weight percentage of rGO were incorporated with ZnO and the final products are named as  $\text{ZnO}_{\text{rGO-1}}$ ,  $\text{ZnO}_{\text{rGO-2}}$ , and  $\text{ZnO}_{\text{rGO-3}}$ . The as-prepared pristine ZnO and  $\text{ZnO}_{\text{rGO}}$  hybrids were used for degradation of methylene blue (MB) dye in aqueous solution under standard solar light illumination. The results imply that  $\text{ZnO}_{\text{rGO}}$  composites reveal  $\sim 6.3$  times enhancement in degradation constant in comparison to pristine ZnO. The PL peak of  $\text{ZnO}_{\text{rGO}}$  composites is much more reduced when compared to pristine ZnO, signifies that the rGO greatly improves photoinduced charge-transfer efficiency and electron-transfer rate which resulting in the superior photocatalytic activity of the  $\text{ZnO}_{\text{rGO}}$  composites.

## 2. Experimental section

### 2.1. Chemicals

Graphite flakes (+100 mesh), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), nitric acid ( $\text{HNO}_3$ ), zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ), and ethanolamine ( $\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$ ) were purchased from Sigma-Aldrich Chemical Co. All chemicals are analytical reagent (AR) grade and used without any further purification. Deionised water was used throughout the experiment.

### 2.2. Preparation of zinc oxide flowers

In a typical synthesis procedure, 0.44 g of zinc acetate dihydrate was dissolved in 50 mL of water followed by the drop by drop addition of 2 mL of ethanolamine under constant magnetic stirring. The final reaction mixture transferred to the Teflon lined stainless steel autoclave and heated to  $150^\circ\text{C}$  in a programmable oven at the heating rate of  $10^\circ\text{C}/\text{min}$  and maintained at that temperature for 12 h. After, the reaction time, the Teflon autoclave was oven cooled. The white coloured ZnO powder was separated from the solution, washed several times with deionised water and ethanol to remove the residual impurities.

### 2.3. Preparation of zinc oxide-reduced graphene oxide hybrids

Firstly, graphene oxide (GO) was prepared by oxidation of natural graphite powder following modified Hummer's method [34], as described briefly in the supporting information. In a typical (Scheme 1) synthesis procedure of  $\text{ZnO}_{\text{rGO-1}}$ , 0.42 g of zinc acetate dihydrate and 8 mL ( $\sim 1$  mg/mL) of as-prepared graphene oxide were ultrasonically dispersed in 30 mL of water flowed by the slow addition of 2 mL of ethanolamine. The resulting final mixture was transferred to a Teflon-lined autoclave and maintained at  $150^\circ\text{C}$  for 12 h. After natural cooling to room temperature, the as-synthesized products were washed thoroughly with distilled water, ethanol and acetone to remove the residual impurities. The other  $\text{ZnO}_{\text{rGO}}$  composites were prepared by employing similar protocols, except varying the weight ratio of zinc acetate dihydrate and graphene oxide. The detailed reaction conditions are summarized in Table 1.

### 2.4. Details and experimental procedure for photocatalytic studies

In a typical photocatalytic reaction, 50 mg of as-prepared photocatalytic material was ultrasonically dispersed in a 50 mL of aqueous methylene blue (MB) ( $1 \times 10^{-4}$  M) in a quartz reactor. The solution was magnetically stirred for 60 min in dark to saturate adsorption/desorption of MB solution on a catalyst. After 30 min of stirring, the solution was irradiated with UV-Vis light (300 W Mercury-Xenon lamp) accompanied by proper stirring to ensure uniform exposure of the suspension throughout the process. The reactor temperature is maintained low by circulating cold water.

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