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# Single-step sensitization of reduced graphene oxide sheets and CdS nanoparticles on ZnO nanorods as visible-light photocatalysts

Rajendra C. Pawar, Caroline Sunyong Lee*

*Department of Materials Engineering, Hanyang University, Ansan 426-791, Gyeonggi-do, South Korea*

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ABSTRACT

Novel composite photocatalysts composed of reduced graphene oxide (RGO) sheets, CdS nanoparticles (CNPs), and ZnO nanorods were developed using a simple low-temperature chemical approach. The RGO sheets and CNPs were sensitized via single-step chemical bath deposition at 70 °C. Because of the incorporation of RGO into the CdS and ZnO structures, the photodegradation performance toward methylene blue (MB) degradation under visible light illumination was significantly improved compared with that of just CdS and ZnO. The highest kinetic rate constant ($k = 0.028\ min^{-1}$) using 0.20 wt% of added RGO was four times higher than that without graphene. This composite degraded MB within 40 min. Such improved performance resulted from effective separation of electron-hole pairs by the RGO sheets. Photoluminescence quenching, increased optical absorbance, and high specific surface area ($23.08\ m^2\ g^{-1}$) also contributed to the high degradation efficiency. An energy level diagram was constructed to explain how the RGO sheets minimized the recombination rate. The developed RGO–CdS–ZnO composites have a potential application in water purification devices.



## 1. Introduction

Heterogeneous photocatalysts play crucial roles in advanced water purification devices because of their broad applicabilities and better performances compared to homogeneous catalysts [1,2]. Among the photocatalysts, ZnO has been shown to be promising because of its high electron mobility at room temperature ($155\ cm^2\ V^{-1}\ s^{-1}$), rich family of nanostructures, non-toxicity, low cost, and a bandgap that is similar to that of $TiO_2$ [3–6]. Despite their good performances and stabilities, ZnO-based photocatalysts have limited applications because of a wide bandgap energy (3.37 eV) and high recombination rate. Hence, various research groups have tried to improve its photocatalytic activity using different approaches such as element doping, sensitization with a visible bandgap semiconductor, and use of gold (Au) nanoparticles [7–10]. Cho et al. developed visible (VIS) and ultraviolet (UV) photocatalysts based on a ZnSe-sensitized ZnO composite [11]. Kundu et al. explored the high absorptivity of ZnO nanorods sensitized with CdS particles and showed that the particle density coverage was important for increasing photocatalytic activity [12]. Yan et al. synthesized a ZnO/$TiO_2$ core-brush structure and demonstrated that an interaction effect can reduce the recombination rate [13]. Han et al. compared the photocatalytic performance of ZnO nanorods and flowerlike structures and observed that the latter exhibited superior activity because of high surface areas and direct electron transport through branches [14]. Lai et al. reported that the larger oxygen vacancies in flowerlike ZnO led to a higher reaction rate and catalytic activity toward rhodamine B photodegradation [15]. Eskizeybek et al. reported an improvement in photodegradation efficiency in sunlight with ZnO nanostructures and polyaniline composites [16]. Bizarro studied Al-doped ZnO nanostructures and found that photocatalytic activity was affected by surface morphology [17]. Udawatte et al. synthesized Au/ZnO nanoparticle composites to minimize the photoelectron recombination rate [18]. However, these combinations suffered from low catalytic performance, low visible light absorptivity and stability, and high cost.

Recently, low bandgap semiconductor sensitization has been reported as the best option spanning the UV as well as the VIS portions of the solar spectrum [19,20]. A low bandgap semiconductor can potentially use multiple electron-hole pair generation per incident photon to achieve higher photocatalytic activity [21]. Various researchers have proposed visible-bandgap semiconductors for effective sensitization, such as CdSe, InP, CdTe, PbS, and CdS [22–26]. Among these sensitizers, CdS is highly promising because of its reasonable bandgap (2.42 eV), which offers new opportunities for light harvesting. Recently, our group reported CdS-sensitized ZnO nanorods synthesized using a chemical bath deposition method and their use in a solar cell application [27]. Wang et al. improved the stability and catalytic activity

* Corresponding author. Tel.: +82 2314004697.
*E-mail addresses:* sunyonglee@hanyang.ac.kr, sunyong523@gmail.com (C.S. Lee).

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by synthesizing a CdS–ZnO core–shell structure using a modified hydrothermal method [28]. Li et al. used a simple two-step process to prepare CdS–ZnO heterostructure photocatalysts having improved performance because of low recombination rates [29]. Although these had satisfactory photodegradation performance, it was not sufficient for commercial photocatalytic devices. Improving the photocatalytic efficiency is essential by avoiding recombination losses and promoting fast electron transportation.

With the discovery of RGO, a wide range of potential applications was expected because of its remarkable properties including high electron mobility at room temperature, large theoretical specific surface area ($2630\,m^2\,g^{-1}$), excellent thermal conductivity ($3000–5000\,Wm^{-1}\,K^{-1}$), good optical transparency (97.7%), and high Young's modulus (~1 TPa) [30]. RGO has been combined with various semiconductors including ZnO, CdS, $TiO_2$, $Fe_3O_4$, $SnO_2$, $Cu_2O$, and $WO_3$, and its use has been explored in supercapacitors, solar cells, gas sensors, batteries, and photocatalysts [31–34]. It plays a crucial role in photocatalysis for the effective separation of photogenerated electron-hole pairs because of its electron-capturing ability [35]. RGO may also be effective for the photodegradation of water pollutants, and methylene blue (MB) dye can be used as a test pollutant. We investigated the incorporation of RGO into CNPs and ZnO nanorods for the effective photodegradation of MB dye in visible light. A unique low-temperature, water-based method for the single-step sensitization of RGO and CdS on ZnO nanorods is described in this paper.

We measured the photocatalytic performance in visible light of composites composed of RGO, CdS, and ZnO. RGO sheets and CNPs were coated onto the surface of ZnO nanorods at 70 °C. We varied the weight percentage of RGO to study its effect on the photocatalytic activity of the CNPs and ZnO nanorods. We correlated the optoelectronic properties of the composites to their photocatalytic activities. A schematic diagram describing the electron transport through the RGO–CdS–ZnO composites was constructed based on these studies.

## 2. Experimental details

### 2.1. Preparation of ZnO nanorods

ZnO nanorods were grown using an aqueous chemical process. A uniform ZnO buffer layer was deposited onto ultrasonically cleaned glass and fluorine-doped tin oxide (FTO)-coated glass substrates. The seed solution was prepared in absolute ethanol from 0.05 M zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$, 99.5%) and 0.05 M diethanolamine ($HN(CH_2CH_2OH)_2$, DEA, 99.5%). The clean substrate was dip-coated for 10 s in the seed solution and then dried overnight at room temperature. The dried films were annealed at 400 °C for 5 min in air to provide a buffer layer of ZnO on the substrate. This coating process was repeated twice to ensure uniform coverage. The buffer layer-coated substrate was then placed vertically in 200 mL of 0.05 M zinc acetate and 0.05 M hexamethylenetetramine (HMTA), and refluxed at 95 ± 3 °C for 5 h. This formed a coating of ZnO nanorods on the substrate.

### 2.2. Preparation of reduced graphene oxide

A modified Hummers method was used to prepare graphene oxide (GO) powders [36]. In brief, 2 g of graphite flakes was added to 100 mL of sulfuric acid ($H_2SO_4$) with constant stirring at a temperature below 10 °C. Then 8 g of potassium permanganate ($KMnO_4$) powder was gradually added at the same temperature, followed by 2 h of constant stirring. Then the mixture was stirred for 1 h at room temperature. The mixture was cooled in a low temperature bath to below 10 °C and subsequently diluted with 100 mL of distilled water. Hydrogen peroxide ($H_2O_2$, 30%, 20 mL) was added to the mixture to dissolve residual permanganate. A large amount of bubbles were released and the color of the mixture changed to brilliant yellow. The colored suspension was filtered and washed several times with 1 M hydrochloric acid (HCl) and distilled water. The final residue was dried in an oven at 60 °C for 12 h and stored in a vacuum oven. To reduce graphene oxide, 100 mg of GO powder was dispersed by ultrasonication for 1 h in 100 mL of distilled water. Then 20 μL of hydrazine monohydrate was added and the solution was refluxed at 90 °C for 2 h. The refluxed solution was filtered and the powder was collected in a glass Petri dish. The Petri dish containing the reduced graphene oxide was kept in an oven at 60 °C for 12 h and then then stored in a vacuum oven. The RGO powder turned black when it was dispersed using ultrasonication in distilled water as it oxidized back to graphene oxide.

### 2.3. Sensitization of ZnO nanorods with RGO nanosheets and CNPs

Coating of the ZnO nanorods with RGO sheets and CNPs was done in one step using a chemical bath deposition method. Initially, an optimized amount of RGO was dispersed by ultrasonication in 80 mL of distilled water over 1 h at room temperature. Then cadmium sulfate (0.005 M) and thiourea (0.005 M) were added into the graphene dispersion with stirring and the pH of the solution was adjusted to 11 using ammonia. Then, the film with the ZnO nanorods was immersed in the solution and stirred for up to 5 h at 70 °C. The substrate now coated with a film of CdS- and RGO-sensitized ZnO nanorods was removed from the bath and rinsed in

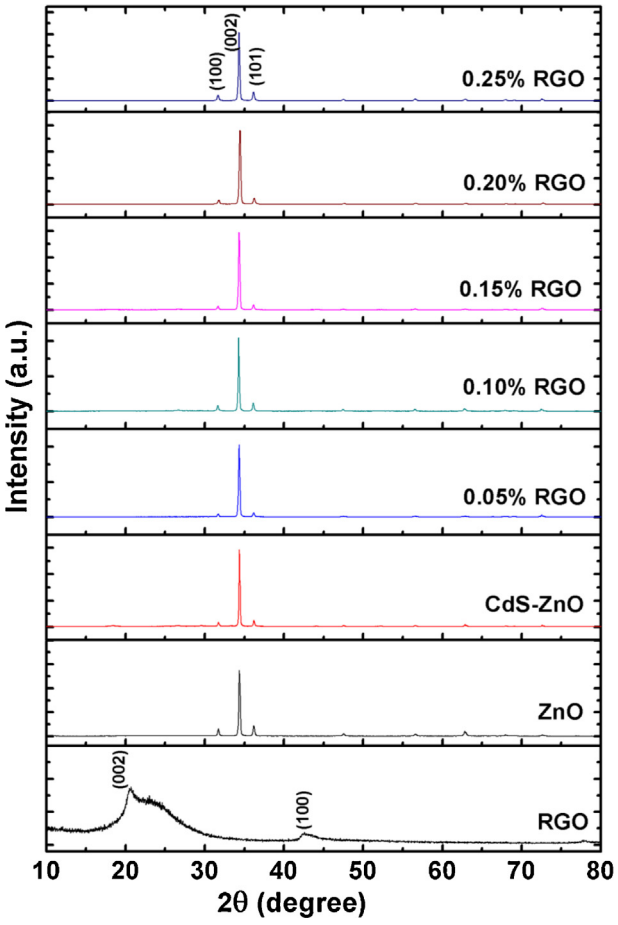


**Fig. 1.** XRD patterns of RGO, ZnO nanorods, CdS-sensitized ZnO nanorods, and RGO–CdS–ZnO composites.