



# A simple, one-pot, low temperature and pressure route for the synthesis of RGO/ZnO nanocomposite and investigating its photocatalytic activity



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## ABSTRACT

A simple, low temperature and pressure, catalyst-free reflux method was reported for the synthesis of reduced graphene oxide (RGO)/ZnO nanocomposite (NC). Formation of ZnO Nanoparticles (NPs) on the surface of Graphene oxide (GO) sheets was led to reduction of GO and fabricating RGO/ZnO NC. The photoluminescence (PL) analysis showed two broad and intense peaks in PL spectra of ZnO and RGO/ZnO samples which are assigned to the electronic transition from zinc interstitial levels ( $I_{Zn}$ ) to Zinc vacancy levels ( $V_{Zn}$ ) and from conduction band to the oxygen vacancy levels (VO), respectively. Broad and intense peaks in PL spectra of ZnO NPs synthesized by our method makes many photogenerated e-h pairs in trap levels due to large number of trap levels. Hybridizing ZnO NPs with GO considerably improve photocatalytic activity of samples due to transferring these electrons to GO sheets and preventing e-h recombination. XRD and FT-IR analyses confirmed that the as-obtained NC is in the form of RGO/ZnO instead of GO/ZnO. Synthesizing NCs by this route largely enhanced photocatalytic activity of NCs, because this synthesis route generates many trap state energy levels such as  $V_O$ ,  $V_{Zn}$  and  $I_{Zn}$  subband energy levels in the band gap of ZnO NPs. These numerous trap states -compared to that of RGO/ZnO NCs obtained by other methods- play an important role in the photocatalytic performance of synthesized NCs by enhancing the visible light absorption due to the resulting ZnO band gap narrowing.

## 1. Introduction

Graphene is a monolayer of  $sp^2$  bonded carbon atoms with a two-dimensional honeycomb structure [1]. Graphene is a promising material for supercapacitors, energy storage, spintronics, catalysis, electronics, antimicrobial and sensor applications [2–5] due to its unique physical and chemical properties such as high electrical and thermal conductivity, high mechanical strength and optical absorptivity [6–11]. During recent decade, reduction of Graphene oxide (GO) has attracted immense interests as an important effective way for graphene production. GO is a few layer of graphite with various oxygen-containing functional groups such as epoxy, hydroxyl, carboxyl and carbonyl which make it hydrophilic and expand the interlayer distance compared to graphite [12,13]. Several methods are employed to reduction of GO which include thermal reducing (such as thermal annealing [14], microwave [15] and photo-reduction [16]) and chemical reduction (such as solvothermal [17], hydrothermal [18], chemical reagent reduction [19] and electrochemical reduction [20]). In many of them, the main aim is to reduce the cost of synthesis. Long reaction time and long temperature-process are the characteristics of the reported approaches. Moreover in many of them toxic materials is produced which is harmful

for health and environment [14–20].

Zinc oxide (ZnO) is a semiconductor with wide band gap, non-toxicity, suitability for doping [21]. Among ZnO nanostructures, ZnO nanoparticles (NPs) are of special interest due to and their wide range of applications in electronic devices, luminescent materials, sensors, fuel cells, anti-bacterial action and photocatalysts [21–26].

ZnO NPs can improve electronic, optoelectronic, photoelectronic and photocatalytic properties of GO and simultaneously reducing it because of interaction between graphene and ZnO nanostructures due to synergic effect in GO and ZnO applications [27–29].

Various methods were reported for synthesis of reduced graphene oxide (RGO)/ZnO nanocomposites including electrochemical deposition [30], microwave [31], ultrasound [32], UV-assisted photocatalytic [33], hydrothermal [34,35], photo-reduction [36] and chemical reduction with reducing agents [37]. However, most of reported methods for synthesis of RGO/ZnO nanocomposites need high reaction temperature and produce toxic by-products. Furthermore, in the most of reported works, ZnO nanoparticles prepared separately and then added to the GO solution which limits its large scale production [30–37]. So it is very important to find a simple, cost effective, one-pot and low temperature method for the fabrication of RGO/ZnO nanocomposites.

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There are several reported hydrothermal methods for synthesizing RGO/ZnO NCs which include complex instruments such as autoclave with high pressures, making it an unsafe and expensive approach. For example, Kavitha et al. reported the growth of ZnO nanomaterials on GO by a hydrothermal method using a Teflon-lined stainless steel autoclave. Acetic acid, zinc acetate and GO were used as precursors and the solution heated at 100 for 7 h in a Teflon-lined stainless steel autoclave [38]. Long and co-workers synthesized ZnO/RGO NCs using an autoclave hydrothermal method and used hydrazine as reducing agent. They added hydrazine to the mixture of GO and zinc nitrate and transferred the solution into a 30 ml Teflon-lined stainless steel autoclave and heated to 140 °C for 4 h [39]. Li et al. prepared ZnO/rGO nanocomposite using a one-pot hydrothermal method using autoclave. They added potassium hydroxide to the solution of GO and zinc chloride and heated it to 180 °C for 1 h in a Teflon-lined stainless steel autoclave [40]. Kang and co-workers used zinc nitrate and GO and PVP as precursor and surfactant, respectively. Final solution was allowed to react at 180 °C for 36 h in a autoclave [41]. Feng et al. used zinc acetate and GO as precursors and transferred final solution to Teflon-lined stainless steel autoclave and heated it to 180 °C for 12 h [42]. Dong et al. fabricated ZnO/RGO NCs using a two-step hydrothermal method using autoclave. They used GO and ZnO nanoparticles as precursors and ammonia and hydrazine hydrate as reducing agent. The resultant solution heated at 180 °C for 10 h in a stainless steel autoclave [43].

In this work, a simple, one-pot, low temperature and pressure, catalyst-free method was reported for the synthesis of RGO/ZnO NC. Synthesized NCs by this method are flexible because of low-temperature process that makes it suitable for flexible substrates. The novel aspect of this work is in fabricating RGO/ZnO nanocomposite via a low temperature and pressure, cost-effective approach. Synthesizing NCs by this route also largely enhance photocatalytic activity of NCs, because this synthesis route generates many trap state energy levels such as  $V_o$ ,  $V_{zn}$  and  $I_{zn}$  subband energy levels in the band gap of ZnO NPs. These numerous trap states -compared to that of RGO/ZnO NCs obtained by other methods- play an important role in the photocatalytic performance of synthesized NCs. These trap state levels serve to increase the visible light absorption due to the resulting ZnO band gap narrowing and RGO reduce the recombination rate according the fact that work function of Graphene is lower than ZnO conduction band [44].

Synthesized Nanocomposites were characterized using Fourier transform-infrared (FT-IR), X-ray diffraction (XRD), Scanning electron microscope (SEM), Photoluminescence (PL), UV-Vis and Raman spectroscopy analyses. Photocatalytic activities of as-prepared nanocomposites is studied by analyzing the photodegradation of Methyl orange (MO), Rhodamine B (RB) and Ni(II) under a 250 W high pressure mercury lamp.

## 2. Experimental

### 2.1. Materials

Zinc acetate dehydrate ( $Zn(CH_3COO)_2 \cdot 2H_2O$ ), Thioglycolic acid (TGA), Sodium hydroxide (NaOH), Graphite fine powder extra pure,  $H_2SO_4$  (98%),  $H_2O_2$  (30%),  $KMnO_4$  and HCl (33%), were purchased from Merck chemical Company.  $KMnO_4$  and HCl (33%) were purchased from Merck Company. Acetone was purchased from Sigma-Aldrich Company. All reagents were of analytical grade and were used without further purification.

### 2.2. Preparation of graphite oxide

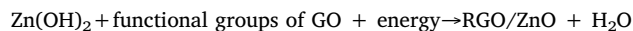
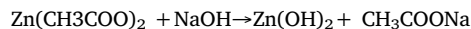
Graphite flakes were oxidized using modified hummers method oxide was prepared by hummers method as we described in our previous work [11]. An amount of 5.2 gr of graphite powder with 57 ml of 98% sulfuric acid and 5.1 g  $NaNO_3$  were mixed and stirred for 60 min in an ice bath. Then 8 g  $KMnO_4$  was added slowly within two hours to the

mixture. The temperature of the mixture was subsequently raised to 35 °C and maintained for 2 h and its color turned from dark green to brown. Then the mixture was stirred for another 30 min at 93 °C. This was followed by the addition of 200 ml of deionized water and 25 ml of  $H_2O_2$  to stop the oxidation reaction, which turned the mixture into bright yellow immediately. The mixture was then washed with water and HCl 5% for three times and again with deionized water using centrifuge until the mixture reached 6.5 pH. This suspension was poured into a crystallizing dish and dried for 24 h at 63 °C.

### 2.3. Synthesis of RGO/ZnO

Firstly, a suspension was obtained by 30 min sonication of 0.1 gr of the dried GO in 60 ml of deionized water. Then 0.065 g Zinc acetate and 0.05 ml TGA dissolved in 60 ml deionized (DI) water followed by stirring for 10 min, to form zinc acetate-TGA complex. Obtained solution and a few drops of 1 M NaOH were added to the suspension. Secondly, final mixtures were transferred to a sealed two-neck, round-bottom flask instead of autoclave. One neck was sealed by a balloon and the other one was connected to the source of Argon gas via vacuum tubing. After evacuating the flask and balloon, Argon gas was injected into the flask to provide enough inert atmospheres. Finally the flask was dipped in a temperature-controlled oil bath under stirring at 90 °C for 10 h.

Functional groups of GO provide active sites for nucleation and growth of ZnO NPs.  $Zn(OH)_2$  can react with oxygen-containment groups of GO for formation of ZnO NPs on the GO surface and reduction of GO [45]. The related reactions are mentioned below:



Solution was centrifuged and further washed with acetone and DI water. The obtained NPs dried in air at room-temperature and final products were collected for characterization.

### 2.4. Photocatalytic activity evaluation

A self-assembled apparatus with a 250 W high pressure mercury lamp as UV irradiation source was used to evaluate the photocatalytic performance of GO, RGO and RGO/ZnO samples by monitoring the degradation of methyl orange (MO), Ni(II) and Rhodamine B (RhB) solutions as pollutant. 2 mg of the GO, RGO and RGO/ZnO NCs were dispersed in 50 ml pollutant aqueous solution under ultrasonic stirring for 15 min. The prepared solution was continuously stirred for about 10 min in the dark to ensure the establishment of adsorption-desorption equilibrium before UV irradiation. Photocatalytic experiments were designed to compare the photoactivity of the ZnO, GO, RGO and RGO/ZnO NCs under UV irradiation. The samples were taken out at the specific intervals of exposure time and their variation of pollutant concentration was measured by monitoring the changes in the absorption intensity using UV-Visible spectrometer (Ava Spec-2048 TEC).

### 2.5. Characterization

Infrared absorption data were obtained by using a Fourier-transform-infrared (FTIR) spectrometer. X-ray diffraction (XRD) was performed by an advanced d8 Bruker system using  $Cu-k_\alpha$  radiation of wavelength  $\lambda = 0.15406$  nm. The specific surface area was obtained by nitrogen adsorption/desorption based on Brunauer-Emmett-Teller (BET) method using a Micromeritics TRISTAR II 3020 instrument. UV-visible (UV-Vis) and photoluminescence (PL) spectra were carried out using an Avantes spectrometer (Ava Spec-2048 TEC). PL studies were performed under UV-254 nm excitation. The scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) spectra were taken using JEOL JSM 6390 LV scanning electron microscope, operating at an accelerating voltage of 15 kV.

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