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Research paper

Synthesis of reduced graphene oxide sheets decorated by zinc oxide nanoparticles: Crystallographic, optical, morphological and photocatalytic study

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ABSTRACT

Reduced graphene oxide (RGO) sheets decorated by ZnO nanoparticles were synthesized using wet impregnation method. The composite material was characterized by means of X-ray diffraction (XRD), Williamson-Hall Plot (W-H Plot) and Scanning Electron Microscope (SEM) analysis. The XRD pattern revealed orderly hexagonal (wurtzite) structure of the ZnO nanoparticles. Surface morphology of ZnO, RGO and RGO-ZnO was investigated using SEM analysis. SEM images indicated the uniform distribution of ZnO onto the RGO surface. The photocatalytic activity of nanocomposite was demonstrated by determining the degradation of methylene blue dye. The degradation of dye took place due to efficient electron-hole recombination of photo-induced electrons. Finally, plausible mechanism was explained with the help of scavengers. Overall, wet impregnation method was found efficient to produce RGO with uniform ZnO loading. The prepared RGO-ZnO composite can efficiently degrade the dye under UV radiation.

1. Introduction

Extremely high emission of organic pollutants has been observed in last two decades as an effect of increase in industrialization and population. These two issues are found to be responsible for potential discharge of organic pollutants from industries like textile, printing, petroleum, pesticides, paint and pharmaceuticals, etc. Some of the most insidious and destructive pollutants are synthetic dyestuff, benzene hydrocarbons, sulphonamides, phthalates, aromatic nitro compounds and phenols. These pollutants are found to be detrimental because of their carcinogenic nature [1]. Their removal from industrial effluent is one of the main concerns for chemical industries/environmental protection agencies. In recent years, conventional treatment methods such as biological treatment methods, physical and physico-chemical treatment methods have been investigated for the removal various pollutants from industrial and domestic wastes [2].

Among available techniques, heterogeneous photocatalysis has enormous potential to treat wide range of pollutant and the possible use of solar energy during treatment [3]. Further, several studies have investigated the degradation of organic pollutants using heterogeneous photocatalysis [4–6]. This may be due to the fact that the photo catalytic activity of metal oxide as a result of higher surface area and surface defects. In this context, some of the research articles reported the application of various metal oxide semiconductors such as TiO_2, Nb_2O_5, Cu_2O, and ZrO_2 as a photocatalysts [7–10]. Among various photo catalysts, ZnO is reported as one of the promising catalyst for the treatment of contaminated water due to its superior properties like low cost, abundance, non-toxicity and high surface activity [11]. Fast recombination of electron-hole pair in ZnO is one of the limiting factors in photocatalytic process. There have been various methods reported to improve the photocatalytic activity of ZnO [12,13]. Recently, coupling with other semiconductors [14,15] and doping with metals [16,17], non-metals [18], rare earth metals, etc. [19,20] were proposed to improve photocatalytic activity of ZnO.

Graphene oxide (GO) has attained great deal of interest due to higher surface area, because of exfoliation. Graphene was also been employed to prepare a photo catalyst composite because of its

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extraordinary properties. These properties include unique two-dimensional structure, high electron conductivity, high surface area and excellent chemical stability [21,22]. Effective charge separation, extended photo-response and high pollutant adsorption capacity of graphene can enhance the photocatalytic performance of graphene-based photocatalysts nanocomposite [21–23].

Graphene oxide exhibit a much higher surface area and it can act as an attractive alternative adsorbent than conventional adsorbents, such as activated carbon and mesoporous carbons. Organic pollutant molecules and cations can be effectively adsorbed by using graphene oxide, due to its highly acidic nature of the components present on the surface. A composite of GO with other nanoparticles can be greatly enhance the adsorption efficiency. Hu et al. reported a highly effective solar photocatalyst consist of reduced graphene oxide supported bismuth ferrite synthesized via a facile co-precipitation method at a low temperature of 95 °C [24].

It is of great interest to study the possibility of graphene complex oxide nanocomposites, such as RGO/ZnO systems for the degradation of organic pollutants. To the best of our knowledge, no report is available on the structural properties of RGO-ZnO nanocomposites. In this article, impregnation method was followed to prepare RGO-ZnO composite. The present study attempts to synthesize a RGO-ZnO composite which possess the unique property of photocatalyst. The photocatalyst is further characterized to understand the surface morphology. The possible application of composite in dye degradation is also discussed in detail.

2. Materials and methods

2.1. Materials

For the synthesis of ZnO nanoparticles, analytical grade zinc nitrate (Zn $(NO_3)_2$ $6H_2O$, >98% pure) and fuel citric acid ($C_6H_8O_7H_2O$, >98% pure) was purchased from Merck, India. For the synthesis of RGO, graphite powder has been procured from MDB Chemicals Pvt. Ltd. Jalgaon MS India. Millipore deionised water was used throughout the experimentation. All the chemicals were used as it is received from the supplier without further purification.

2.2. Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized using sol-gel combustion technique [25]. In brief, it begins with dissolution of zinc nitrate (Zn $(NO_3)_2$ $6H_2O$) and citric acid ($C_6H_8O_7H_2O$) in distilled water. Aqueous solution of metal nitrate to citric acid was used in 1:1 M ratio. The solution was placed in a pre-heated muffle furnace at 350 °C for about 30 min. Finally the resultant solution is transformed into a transparent gel. It was ignited to initiate auto combustion reaction. The solution was left overnight to cool down to room temperature. The white powder obtained after grinding was calcined at 400 °C for four hours.

2.3. Preparation of graphene oxide

Graphene oxide was prepared by using modified Hummer's method [26]. Graphite powder (1 g) and $NaNO_3$ (1 g) were added into concentrated H_2SO_4 (140 mL) under agitation. Then $KMnO_4$ (3 g) was added slowly (drop wise) to the above solution under ice bath to maintain the temperature less than 20 °C in order to prevent overheating. Then the mixture was agitated at 40 °C for 5 h followed by dilution with deionised water. The above reaction was completed by the addition of 30% H_2O_2 solution till the colour of solution transferred to brilliant yellow. The resulting mixture was washed with acetone and deionised water respectively, followed by filtration and drying. The obtained graphite oxide was subjected to sonication for 30 min in water-ethanol solution to obtain GO sheets.

2.4. Preparation of ZnO/RGO nanocomposites

In a typical experiment 0.5 g graphene oxide and 0.1 g polyvinylpyrolidone (PVP) was dispersed in 500 mL deionised water to form graphene oxide solution. Then, 0.5 g ZnO nanoparticles were added into graphene oxide solution and mixture was agitated at room temperature for 2 h. The resultant precipitate was separated by using centrifugation and thoroughly washed with deionised water to remove impurities and overnight dried at 80 °C to yield RGO-ZnO composite [27]. The flowchart for the synthesis of RGO-ZnO composite is shown in Fig. 1.

2.5. Photocatalytic experiment

Photocatalytic experiments were performed using 125 W UV lamp as light source placed vertically in batch reactor. The reactor was surrounded by a cooling jacket circulated with water to control the temperature. Schematic diagram of photocatalytic experimental setup is shown in Fig. 2. To begin with the degradation by photocatalysis, initially, 20 ppm of methylene blue (25 mL) was mixed with 0.02 g of catalyst in a 100 mL glass beaker. The prepared solution has been placed at dark for 20 min to reach the

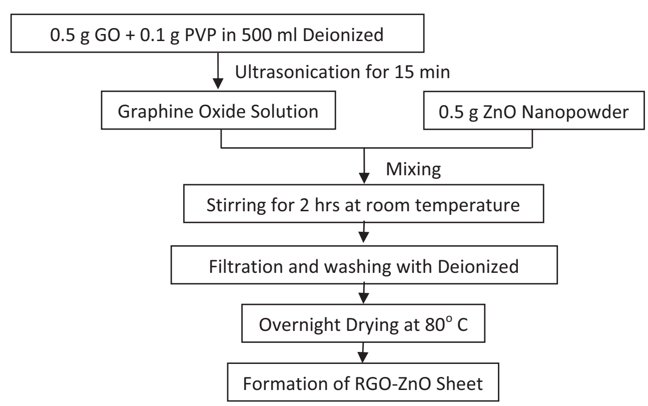

Fig. 1. Schematic diagram of RGO-ZnO composite synthesis.

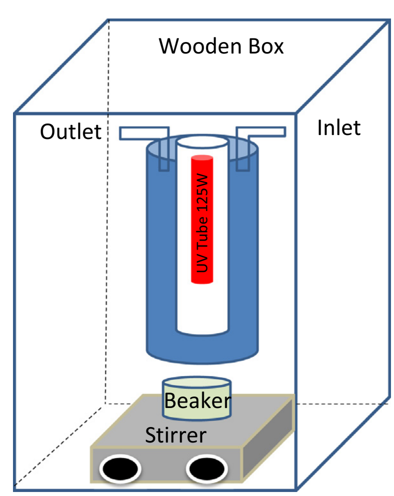

Fig. 2. Schematic diagram of photocatalytic experimental setup.