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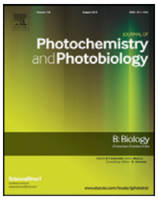

Facile synthesis of zinc oxide nanoparticles decorated graphene oxide composite via simple solvothermal route and their photocatalytic activity on methylene blue degradation☆

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ABSTRACT

Zinc oxide nanoparticles decorated graphene oxide (ZnO@GO) composite was synthesized by simple solvothermal method where zinc oxide (ZnO) nanoparticles and graphene oxide (GO) were synthesized via simple thermal oxidation and Hummers method, respectively. The obtained materials were thoroughly characterized by various physico-chemical techniques such as X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. Raman spectrum shows the intensity of D to G value was close to one which confirms the obtained GO and ZnO@GO composite possesses moderate graphitization. TEM images shows the ZnO nanoparticles mean size of 15 ± 5 nm were dispersed over the wrinkled graphene layers. The photocatalytic performance of ZnO@GO composite on degradation of methylene blue (MB) is investigated and the results show that the GO plays an important role in the enhancement of photocatalytic performance. The synthesized ZnO@GO composite achieves a maximum degradation efficiency of 98.5% in a neutral solution under UV-light irradiation for 15 min as compared with pure ZnO (degradation efficiency is 49% after 60 min of irradiation) due to the increased light absorption, the reduced charge recombination with the introduction of GO. Moreover, the resulting ZnO@GO composite possesses excellent degradation efficiency as compared to ZnO nanoparticles alone on MB.

1. Introduction

In recent years, graphene and its composite materials are attracted enormous attention due their wide range of potential applications in catalysis, solar cells, hydrogen storage, nanoelectronics, sensors and nanocomposites [1–6]. Graphene is an allotrope of carbon with two-dimensional honeycomb sp^2 crystalline lattice and good conductivity. The hexagonal atomic structure of graphene is able to supply a building platform for the epitaxial growth of other hexagonal nanostructures such as zinc oxide (ZnO), TiO_2 and SnO_2. In addition, graphene based semiconductor composites greatly improves the photocatalytic properties of these host materials. Among these semiconductor nanoparticles, ZnO received considerable attention of scientists owing to its size and shape dependent photocatalytic properties. ZnO is an n-type semiconductor with bandgap ~3.37 eV, which has been applied in many fields such as photocatalysis, solar cells, gas sensors and photodetectors [7–11]. In general, small size ZnO nanoparticles have increased specific surface area and more numbers of active surface sites where the photogenerated charge carriers are able to react with absorbed molecules. Graphene oxide (GO) with hydroxyl and carboxyl groups, which possesses excellent dispersibility in solvents and thus provides various opportunities for the fabrication of GO-based hybrid composites [12,13].

In general, dyes and pigments are hazardous and toxic to environment as well as for human beings. Upon high discharge of these environmentally unfriendly materials causes ulceration of skin and mucous membrane, dermatitis, perforation of nasal septum, severe irritation of respiratory tract and on ingestion may cause vomiting, pain, haemorrhage and sharp diarrhea [14]. So the degradation of organic dyes finds extensive application for environmental safety. The photocatalytic degradation is one of the best methods for detoxification of dyes and pollutants [15]. This process can mineralize organic dyes completely to H_2O, CO_2, and other nontoxic compounds without

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☆ Electronic Supplementary Information (ESI) available: XRD pattern of graphite powder and graphene oxide, UV–Vis spectra of MB with ZnO nanoparticles and degradation efficiency (%) of ZnO nanoparticles on MB.

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causing a secondary pollution [16,17]. Methylene blue (MB) is a thiazine dye and finds various applications in medicine, biology and analytical chemistry. Owing to the solubility of MB in polar solvents such as water and ethanol, the effluents of those industries contain MB, which is toxic for aquatic organisms, nitrifying bacteria and fishes [18]. Therefore the degradation of MB is environmentally significant. Many researchers have been studied the degradation of MB as a model reaction for proving the photocatalytic ability of synthesized nanomaterials [19,20]. Various techniques have been adopted to synthesis photocatalytic ZnO nanoparticles and ZnO nanoparticles decorated graphene based nanostructured materials. However, it is a challengeable task to synthesize the nanomaterials with controlled particle size without agglomeration for better photocatalytic activity [21–26].

In our work, zinc oxide nanoparticles decorated graphene oxide (ZnO@GO) composite has been prepared as a photocatalyst for the organic dye degradation. The zinc oxide (ZnO) nanoparticles were synthesized by simple thermal oxidation utilizing horizontal tubular furnace. GO was synthesized by Hummers method. The synthesized ZnO nanoparticles were impregnated over the GO sheets (layers) by simple solvothermal process. Moreover, the obtained ZnO@GO composite was used to enhance the photocatalytic performance on MB. The optical property was revealed by ultraviolet-visible (UV–Vis) spectroscopy techniques. The results show that the ZnO@GO composite plays an important role in the enhancement of photocatalytic performance and achieves a maximum degradation efficiency in a neutral solution under UV-light irradiation of 15 min as compared to pure ZnO nanoparticles due to the increased light absorption, the reduced charge recombination with the introduction of GO.

2. Experimental

2.1. Materials

Graphite powder (GP), zinc powder (<50 nm) and MB were purchased from Sigma Aldrich. Potassium permanganate, barium chloride, hydrogen peroxide, sulfuric acid, hydrochloric acid, tetrahydrofuran, acetone, oxygen gas and hydrogen gas were purchased from Ducksan chemicals. The entire chemicals were used without any further purification. The deionized (DI) water was used throughout this study.

2.2. Synthesis of ZnO

ZnO nanoparticles were synthesized using zinc powder by the simple thermal oxidation method with help of horizontal tubular furnace [27]. Typically, an appropriate amount of zinc powder (the mean size was <50 nm) was placed in a quartz boat and inserts into the middle of quartz tube at the time of reaction temperature (800 °C) with heating rate of 10 °C/min. Prior to insert the quartz boat with zinc powder, the tubular furnace was purged under the mixture of argon gas and oxygen gas at the flow rate of 50 and 10 sccm (sccm denotes standard cubic centimeter per minute), respectively. After placing the zinc powder, the reaction temperature was maintained for 30 min. Then the furnace was cooled to room temperature under argon atmosphere, and then final ZnO nanoparticles were collected after the completion of the reaction.

2.3. Synthesis of GO

The GO was synthesized using the modified Hummers method without any major modification [28]. 100 mL of concentrated sulfuric acid was taken in to a 1000 mL of beaker and it was cooled to 0 °C in an ice-bath as a safety measure. Subsequently 4 g of GP was added in to the sulfuric acid and vigorously stirred for 10 min. While maintaining vigorous stirring, 8 g of potassium permanganate was added slowly to the suspension. The rate of addition was controlled carefully to prevent the temperature of the suspension exceeding from 20 °C. The suspension was stirred for 15 min below 20 °C and then the ice-bath was removed. Then the temperature of the suspension was raised to 40 °C, where it was maintained for 1 h. As the reaction progressed, the mixture gradually thickened with a diminishing in effervescence and the paste was brownish in color. At the end of reaction, 200 mL of DI water was slowly added into the paste and an increase in temperature to 98 °C. The diluted suspension was maintained at this temperature for 30 min. 560 mL of DI water added in to the suspension for further dilution and then 100 mL of hydrogen peroxide (28%) was added to reduce the residual permanganate and manganese dioxide to colorless soluble manganese sulfate. The obtained suspension was centrifuged and residue was thoroughly washed with 5% of hydrochloric acid until aqueous layer could not get salt with barium chloride. The final residue was washed with acetone and the obtained solid was dried at 70 °C for 5 h in a hot air oven under static condition. The dry form of resulted GO was ground well and stored for further use.

2.4. Synthesis of ZnO@GO Composite

An appropriate amount (500 mg) of GO was dispersed in 75 mL of tetrahydrofuran in a 100 mL round bottom (RB) flask. 200 mg of ZnO nanoparticles were added in to the GO dispersion and sonicated for 20 min at ambient temperature. Subsequently the mixture was refluxed (65 °C) for 24 h under static condition. The final mixture was centrifuged and washed with tetrahydrofuran. The residue was dried at 100 °C for 5 h in a hot air oven. The resulting product was collected and used to enhance the photocatalytic acidity on degradation of organic dyes including methylene blue. The schematic representation of the synthesis of ZnO@GO composite was shown in Fig. 1.

2.5. Characterization Methods

The synthesized ZnO, GO and ZnO@GO were characterized by various physico-chemical such as X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy- attenuated total reflectance (ATR), field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), UV–Visible spectroscopy and Raman spectroscopy techniques. The XRD patterns were obtained on a PANalytical X'Pert diffractometer using Cu Kα radiation (K = 1.54 Å) equipped with a liquid nitrogen cooled germanium solid-state detector. The XRD patterns of resulted samples were recorded in the 2θ range of 10–90°, and at the step interval of 0.02° with the counting time of 5 s at each point. The FTIR spectra were recorded in transmittance mode on a perkin elmer spectrum two in the wavenumber range of 400–4000 cm^{-1} by the co-addition of 32 scans at a resolution of 16 cm^{-1}. Raman spectra were recorded with a Raman spectrometer Almega X/Thermo using laser excitation line at 532 nm. FESEM was performed on Hitachi S-4800 at an accelerating voltage of 4 kV. The preparation of samples for FESEM, a small amount of samples was placing on conductive carbon tape. HRTEM images were obtained using a TITAN G2 ChemiSTEM Cs Probe electron microscope operated at 200 kV. Samples for HRTEM were prepared by placing droplets of a suspension of the sample in ethanol on a carbon-coated polymer micro grid supported on a Cu grid. X-ray photoelectron spectroscopy (XPS) was carried out using a K-Alpha spectrometer (Thermo Scientific). The spectra were baseline corrected using the instrument software. UV–Vis spectroscopy analysis was performed using an OPTIZEN 3220 UV.

2.6. Photocatalytic Activity of ZnO@GO Composite on MB

Photocatalytic activity of the synthesized ZnO@GO composite were tested on MB under UV-light and degradation efficiency depends on irradiation time was revealed by using UV–Vis spectrophotometer (OPTIZEN 3220 UV). MB stock solution (1 mmol) was prepared in DI water. The MB solution with absorbance intensity of around 2.1 was prepared from MB stock solution. 50 mL of prepared MB solution