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Cadmium oxide nanoparticles grown in situ on reduced graphene oxide for enhanced photocatalytic degradation of methylene blue dye under ultraviolet irradiation

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ABSTRACT

Cadmium oxide (CdO) nanoparticles (NPs), reduced graphene oxide (rGO) and rGO-CdO nanocomposites have been synthesized using one step hydrothermal method. The structural and optical properties of CdO NPs, rGO, and rGO-CdO nanocomposites were investigated by X-ray diffraction (XRD), energy dispersive X-ray (EDX), high resolution transmission electron microscopy (HR-TEM), Raman spectroscopy (RS), ultraviolet–visible spectroscopy (UV–Vis.) and photoluminescence (PL) spectroscopy techniques. The rGO has a sharp 2D peak compared to GO. The sharp nature of 2D band may be due to the larger contribution from single layer sheet. The photocatalytic activity of the synthesized samples has been investigated under UV irradiation. The results of photocatalytic measurements revealed that ~80% of MB dye is degraded by adding the rGO-CdO nanocomposites as photocatalysts into the dye solution. The decrease in the intensity of emission peaks indicates that the photogenerated charge carriers have been transferred from CdO NPs to rGO sheets, which causes to increase the density of O_2^- and •OH radicals in the dye solution. The CdO nanoparticles gown on the rGO sheets showed enhanced ferromagnetism (FM) at room temperature, which may be attributed to the short range magnetic interaction of magnetic moments of CdO NPs and spin units present on the rGO sheets.

1. Introduction

Graphene is a two dimensional (2D) structure consisting of single layer of carbon atoms [1]. It has been established as a novel material due to its extraordinary large surface area (2630 m^2/g) [2], high electron mobility (200,000 cm^2/Vs) [3], high thermal conductivity (~5000 W/mK) [4], excellent mechanical stability (Young's modulus ~1,100 GPa and fracture strength 125 GPa) [5] and showing interesting transport phenomena such as, quantum Hall effect [6]. These exceptional features of graphene have made it as a promising candidate to be used in various fields of technology such as, energy storage [2], liquid crystal devices [7], transparent electrodes [8] and electromechanical resonators [9]. However, the re-stacking tendency of graphene during reduction process leads to a great loss of effective surface area that limits its wide applications for advancement of the future technology [10]. The aggregation problem can be minimized by decreasing π–π stacking interactions by incorporating the metal NPs on the graphene sheets [11].

CdO is an n-type metal oxide semiconductor with a direct band gap of 2.3 eV and an indirect band gap of 1.36 eV [12]. Recently, CdO NPs have attracted considerable attention of the scientific community due its potential applications in solar cells, flat-panel display and developing new sensing devices [12]. It can also be used as an alternative for electrode material [13]. Graphene based low dimensional metal oxide composites have emerged as a rising star on the horizon of materials science. It has attracted a lot of attention to the world wide scientists due to its ability to combine the properties of graphene and metal oxide NPs. In addition to the technological application, the graphene based metal oxide composites have now been considered as a promising material due to its unique properties and great potential for application in many areas of science and technology, particularly in solving the problems related to energy crisis and environmental issues [11,14,15].

Different type of metal oxide semiconductors such as, tin oxide (SnO_2) [16], titanium oxide (TiO_2) [17] and its composites with rGO [18] have been used widely to degrade organic pollutants. However, in best of our knowledge, the synthesis of rGO-CdO nanocomposites and its photocatalytic activity has not been reported yet. Due to small band gap of CdO compared to other metal oxides such as; TiO_2 (3.0 eV) [19], zinc oxide (ZnO) (3.4 eV) [20], and SnO_2 (3.6 eV) [21], rGO-CdO nanocomposites may act as a potential photocatalyst material for the photodegradation of long organic molecules. The small band gap energy of CdO has made it possible to overcome the need of irradiation of any kind radiation (ultraviolet or visible) for the photodegradation of dye in aqueous solution. In addition to photocatalyst response of rGO-CdO nanocomposites, we would also like to investigate the effect of rGO sheets on room temperature ferromagnetism (RTFM) of

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nanostructured CdO to highlight the hidden potential of such composite materials for the advancement of future technology.

A simple and low cost hydrothermal method has been used to synthesize CdO NPs, rGO, and rGO-CdO nanocomposites. The structural morphology and elemental analysis of the synthesized nanocomposites were studied by XRD, HR-TEM and EDX measurements. The optical properties of the synthesized samples were investigated by UV–Vis., PL and Raman spectroscopy techniques. The magnetic properties of pure CdO NPs and rGO-CdO nanocomposites were also investigated at room temperature using vibrating sample magnetometer (VSM) measurements.

2. Experimental

2.1. Materials and Synthesis

Cadmium acetate dihydrate $Cd(CH_3COO)_2 \cdot 2H_2O$, sulphuric acid ($H_2SO_4$), phosphoric acid ($H_3PO_4$), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30%), hydrochloric acid (HCL), ethanol (C_2H_5OH), hydrazine hydrate (N_2H_4) were purchased from Sigma Aldrich, USA and used without further purification.

One step in-situ hydrothermal method was used to prepare rGO-CdO nanocomposites using GO as precursor for rGO, and cadmium acetate as precursor for CdO. N_2H_4 was used to reduce GO into rGO with simultaneous formation of CdO NPs on the rGO sheets. The steps involved in the synthesis of rGO-CdO nanocomposites are shown in Fig. 1. In the hydrothermal method, the mixed solution of functionalized GO and metal salts are loaded along with reducing agent in an autoclave for thermal treatment. During thermal treatment, rGO based semiconductor nanocomposites are produced simultaneously by converting GO into rGO. The presence of oxygen containing functional groups like epoxy, carbonyl, carboxyl and hydroxyl on GO are responsible for the uniform and monodispersed anchoring of CdO NPs over the rGO sheets [22].

2.1.1. Synthesis of GO

GO was synthesized using an improved method [23] with some modifications. In general, a mixture of concentrated H_2SO_4 (360 mL) and H_3PO_4 (40 mL) was prepared in a conical flask. The graphite powder (3 g) was mixed slowly into the mixed solution of concentrated H_2SO_4 and H_3PO_4 while stirring. The homogeneous solution was made by vigorous stirring for 15 min. Thereafter, the conical flask containing homogeneous solution of concentrated H_2SO_4/H_3PO_4 and graphite was kept in a water bath and 18 g of $KMnO_4$ was added into the solution very slowly under vigorous stirring at 35 °C. After mixing of $KMnO_4$, the water bath was removed and the resultant solution was then heated to 55 °C and stirred it for 12 h to complete the oxidation process of graphite. During the oxidation reaction, the color of mixed solution turns out to dark brown. The reaction was cooled to room temperature after vigorous stirring for 12 h and thereafter ice (~400 mL) is poured into the solution. The color of solution changes to purple. To stop the oxidation process, 30% H_2O_2 solution was added gradually till the color of the mixed solution turned to bright yellow. The obtained slurry was centrifuged at 4000 rpm for 1 h, and the supernatant was removed. The precipitate was then washed with 200 mL of water, 200 mL of 30% HCl, and 200 mL of ethanol in succession until a pH 5 of the solution was achieved. The remaining solid material was then dried overnight at 40 °C. The obtained brown solid powder of GO was collected and stored for further use.

2.1.2. Synthesis of rGO

The synthesized brown solid powder of GO (0.02 mg) was first dispersed into 40 mL double distilled water under mild stirring. The dispersed GO was then exfoliated by using ultrasonication for 1 h. 10 μL N_2H_4 was added drop wise into the above mentioned solution under

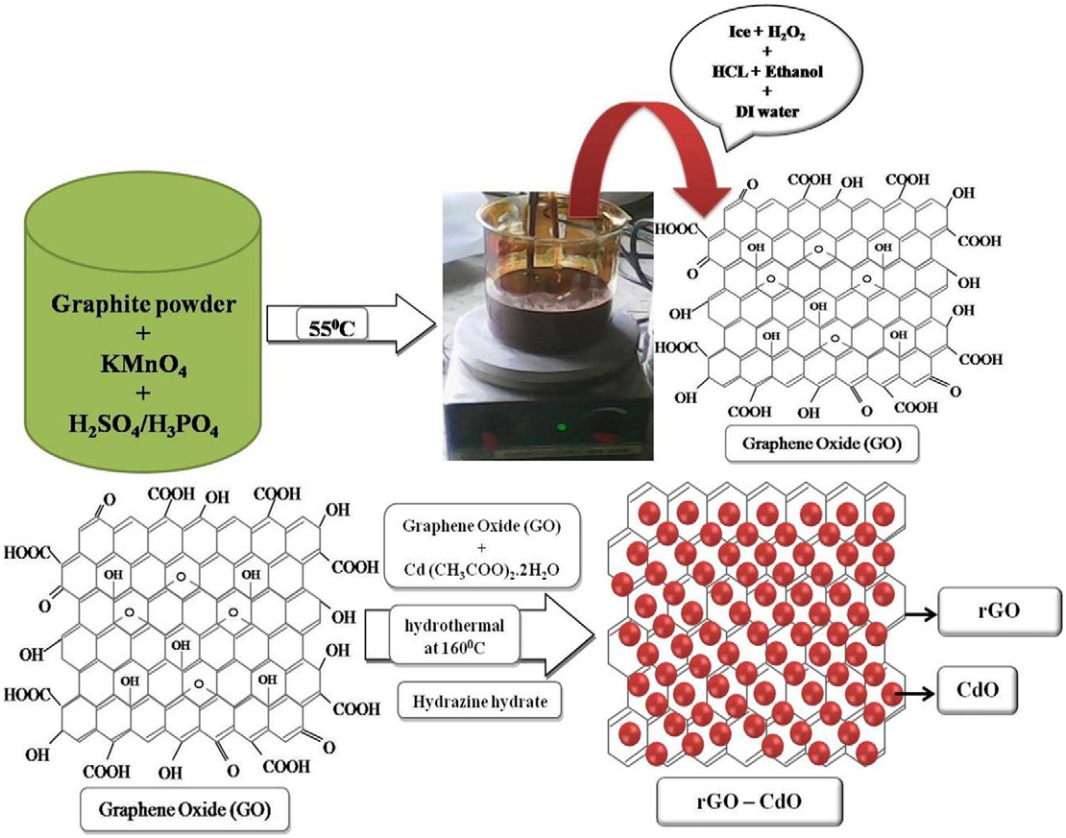

Fig. 1. Graphical illustration of the synthesis of CdO NPs on rGO sheets.