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Synthesis of graphene/zirconium oxide nanocomposite photocatalyst for the removal of rhodamineB dye from aqueous environment

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ABSTRACT

In this study, we have synthesized graphene/zirconium oxide nanocomposites (Gr@ZrO_2-NC) by employing an alkaline method using green sodium hydroxide, as a reductant. The structural, optical, thermal, electrical, and photocatalytic properties of Gr@ZrO_2-NC were studied. The characterization data confirmed that the zirconium nanoparticles (ZrO_2-NPs) were successfully incorporated into the graphene sheets. X-ray diffraction analysis ensured that the ZrO_2-NPs have a monoclinic structure. Thermogravimetric and differential scanning calorimetric analyses revealed that higher thermal stability owing to the strong interaction between ZrO_2-NPs and graphene. The Gr@ZrO_2-NC have also used for the photocatalysis of a Rhodamine B (RhB) dye under aqueous environment. Obtained data showed the efficient removal of RhB dye under UV light irradiation through the production of reactive oxygen species (ROS). The present study could open up promising avenues for substitution of toxic reducing agents for the production of Gr@ZrO_2-NC and their potential environmental applications.

1. Introduction

Graphene is an important rising star in materials and its sheets have the one-atom-thick 2D layer of graphite with carbon atoms arranged in a six-numbered-ring plane [1,2]. Graphene exhibits the distinctive biological, chemical, electrical, thermal and mechanical properties, due to its 2D structure consisting of sp^2-hybridized carbon [3]. Despite large specific area, application of graphene depends considerably on its intrinsic properties such as interlayer spacing and thickness etc [4]. Intrinsic properties of the graphene have been modified through the synthesis of its hybrid nanocomposites with the addition of various kinds of nanomaterials [5]. Graphene-based nanocomposites have been extensively studied in the recent years due to their improved biological, chemical, and physical properties [6,7].

Graphene materials containing nanocomposites offer a potent manner to enhance their application by enabling versatile and tailor-made properties with high performance far beyond those of the graphene. Among them, zirconium oxide (ZrO_2) nanoparticles (NPs) are the most widely electrochemical applications to hybridize with graphene or graphene oxide (GO) [8–12]. The graphene/ZrO_2-NPs nanocomposites frequently exhibit unexpected hybrid properties derived from both constituents and deliver the great potential applications in the field of catalysis [13]. The improved photocatalytic properties of graphene-metal oxide NPs nanocomposite materials have been reported [14–17]. The improved photocatalytic properties of graphene-metal oxide NPs nanocomposite materials are attributed to good electron conduction of graphene [18–21], when graphene composite with metal oxide NPs will improve the charge transfer between the metal oxides and Rhodamine B dye molecules.

Thus, in this work, we have synthesized graphene–ZrO_2-NPs nanocomposites (Gr@ZrO_2-NC) using green sodium hydroxide, as a reluctant and investigated their photocatalytic activity against the Rhodamine B dye under UV light radiation.

2. Materials and methods

2.1. Materials

Graphite fine powder, RhB dye and Zirconium acetate [$Zr(CH_3COO)_2$] purchased from Loba Chemie Pvt. Ltd., Mumbai, India. All chemicals and reagents used were of analytical grade.

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2.2. Methods

2.2.1. Preparation of GO

GO was synthesized from graphite fine powder according to the method of Hummers and Offeman (1953) [22], which involves graphite exfoliation in the presence of strong acids and oxidants. Briefly, ~4 g of graphite powder was mixed with 200 mL of H_2SO_4 and stirred in the ice bucket for 40 min. After that 10 g of $KMnO_4$ was slowly added and again stirred for 1 h under similar conditions. Then, the mixture was stirred at room temperature until it became pasty brownish (Suppl. Fig. S1A). The mixture was subsequently diluted with slowly addition of 400 mL of water and reaction temperature was increased rapidly to 90 °C. The color of the mixture was changed from black to brown after 1 h. Finally, 20 mL of H_2O_2 (30% aqueous solution) was added to complete oxidation reaction and prepared GO was washed twice with 3% of HCl. The obtained GO was harvested by centrifugation at 500 rpm for 10 min and slurry was dried under vacuum.

2.2.2. Synthesis of graphene/zirconium oxide nanocomposites (Gr@ZrO_2-NC)

The synthesis of Gr@ZrO_2-NC was performed in two steps. Firstly, ~1 g of zirconium acetate and 1 g of GO were dispersed into 200 mL of water and subjected to sonication for 30 min. Secondly, 20 mL of 1 M sodium hydroxide solution was added drop-wise into the sonicated precursor mixture. The resultant mixture was stirred for 1 h at 100 °C and the color of precursor mixture was changed into black (Suppl. Fig. S1B) indicates the successfully synthesis of Gr@ZrO_2-NC. The synthesized Gr@ZrO_2-NC harvested by the centrifugation at 5000 rpm for 10 min and pellet was washed with 70% ethanol (Fig. 1A and B). The obtained pellet was dried under vacuum (Fig. 1C) and stored in amber color vials at room temperature under dry and dark conditions until used for further study.

2.3. Characterization of Gr@ZrO_2-NC

Synthesis of Gr@ZrO_2-NC in the beaker was monitored by measuring the absorbance (A) by UV–vis spectrophotometer (Perkin Elmer Life and Analytical Sciences, CT, USA) in the wavelength range of 200–800 nm (Fig. 1 A) [23]. Thin film of Gr@ZrO_2-NC was prepared on the borosilicate glass slide analyzed by light microscope at different magnifications. Scanning electron microscopy (SEM) was performed using the fine powder of synthesized Gr@ZrO_2-NC (Fig. 1C) on a carbon tape in a SEM (JEOL JSM-6510LV, Tokyo, Japan) at an accelerating voltage of 20 kV. The elemental analysis was carried out using the Oxford Instruments INCA x-sight energy dispersive X-ray (EDAX) spectrometer equipped with SEM. Transmission electron microscopy (TEM) of aqueous solution of Gr@ZrO_2-NC was carried out on the JEOL instrument (Tokyo, Japan) with an accelerating voltage of ~150 kV [24]. The light microscope and electrons images were obtained and converted into an enhanced meta file format. The X-ray diffraction (XRD) patterns of Gr@ZrO_2-NC powder sample (Fig. 1C) was recorded on MiniFlex™ II benchtop XRD system (Rigaku Corporation, Tokyo, Japan) operating at 40 kV and a current of 30 mA with Cu Kα radiation ($\lambda = 1.54$ A°). The diffracted intensities were recorded from 5° to 80° at 2θ angles [25]. For the FTIR spectroscopic measurements, Gr@ZrO_2-NC powder (Fig. 1C) was mixed with spectroscopic grade potassium bromide (KBr) in the ratio of 1:100 and spectra were recorded in the range of 400–4000 wave number (cm^{-1}) on Perkin Elmer FTIR Spectrum BX (PerkinElmer Life and Analytical Sciences, CT, USA) in the diffuse reflectance mode at a resolution of 4 cm^{-1}in KBr pellets [26]. Thermal analysis of Gr@ZrO_2-NC powder (Fig. 1C) was measured by thermal gravimetric analysis (TGA)/Differential scanning calorimetry (DSC) (PerkinElmer Life and Analytical Sciences, CT, USA) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere [24,25]. The surface area of GO and Gr@ZrO_2-NC was determined using a Micromeritics, ASAP Instrument using nitrogen as the adsorbent.

Frequency dependent electrical properties of Gr@ZrO_2-NC were performed in the frequency range of 75 kHz to 7 MHz using an LCR meter (Agilent-4285A) [25]. The Gr@ZrO_2-NC pellet was coated on adjacent faces with silver paste, thereby forming parallel plate capacitor geometry. The value of dielectric constant (ε′) is calculated using the formula:

$$\varepsilon' = \mathrm{Cpxd}/\varepsilon_0 \mathrm{A} \tag{1}$$

whereas, ε_0 is the permittivity of free space, d is thickness of pellet, A is the cross-sectional area of the flat surface of the pellet and Cp is the capacitance of the specimen in Farad (F). The complex dielectric constant ε" of the samples was calculated using the following relation:

$$\varepsilon'' = \varepsilon' \tan\delta \tag{2}$$

whereas, tanδ is the dielectric loss tangent which is proportional to the loss of energy from the applied field into the sample (this energy is dissipated as heat) and therefore denoted as dielectric loss. Thus, the loss factor (tanδ) which expresses the ratio of the imaginary part of the dielectric constant of the real part.

$$\tan\delta = \varepsilon'' \big/ \varepsilon' \tag{3}$$

The ac conductivity of the samples was determined using the following relation:

$$\sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan\delta \tag{4}$$

whereas, ω is the angular frequency.

2.4. Assessment of photocatalytic activity

The photocatalytic activity of Gr@ZrO_2-NC was assessed using the RhB dye under UV light irradiation (365 nm) [25]. In the photocatalytic experiment, 50 μg/mL of Gr@ZrO_2-NC catalyst (Fig. 1C) was added to 50 mL of dye solution (10 μg/mL). Before irradiation, the suspension containing RhB dye and Gr@ZrO_2-NC was magnetically stirred in the dark for 60 min to ensure the establishment of an adsorption/desorption equilibrium. At a fixed time interval (0, 30, 60, 120, and 180 min) 5 mL aliquots were filtrated and analyzed by recording variations in the maximum absorption band (λ_{max} ~565 nm) using a UV–vis spectrophotometer (Perkin Elmer Life and Analytical Sciences, CT, USA). The effects on photocatalytic activity of Gr@ZrO_2-NC with respect to the RhB dye concentrations (5, 10, 15 and 20 μg/mL) were also assessed at the fixed time (180 min). The role of active, reactive oxygen species (ROS) generated in the photocatalytic system were confirmed by trapping with *tert*-butyl alcohol ($C_4H_{10}O$) and disodium ethylenediaminetetraacetate dehydrate (EDTA-Na_2; $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$) [25,27]. The photodegradation of RhB dye via the photocatalytic activity of Gr@ZrO_2-NC was calculated following the formula:

$$\text{Photodegradation efficiency}(\%) = \frac{Co - C}{Co} \times 100 \tag{5}$$

whereas, Co is the RhB dye initial concentration before photodegradation and C is the absorbance after the different time intervals.