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Fabrication of highly photocatalytic active anatase TiO_2-graphene oxide heterostructures via solid phase ball milling for environmental remediation

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ABSTRACT

This work projects the synthesis of a series of TiO_2/GO composites using TiO_2 and graphene oxide as precursor materials. The composites were synthesised by simple solid-phase ball milling process without using any solvent or high temperature treatment. The structure of the heterophotocatalyst was characterised by X-ray diffraction, Raman, Fourier transform infrared, UV–Vis, scanning electron microscopy and transmission electron microscopy methods. The results showed that TiO_2 particles are anchored firmly and are decorated on graphene oxide sheets. The photocatalytic performance of TiO_2/GO composites for organic pollutant degradation was investigated with methylene blue (MB) dye as test pollutant. The results reveal much higher photocatalytic activity of anatase TiO_2/GO nanocomposites than that of as synthesised anatase TiO_2 under light irridation with $TiO_2/GO_{0.4}$ composite possessing the highest photocatalytic activity. These photocatalytic reactions followed the pseudo first order kinetics from which rate of reaction was also determined. The possible photocatalytic mechanism of MB degradation by TiO_2/GO composite is discussed.

1. Introduction

In the recent years, the fast pace of industrialisation, population growth, urbanisation, depletion of environmental resources etc. has led to the increased contamination of potable water [1]. Textile and other dye manufacturing industries discharge toxic and non biodegradable dyes such as methylene blue (MB) into the environment. Almost 20% of the total world dye production is lost during industrial processing leading to environmental pollution particularly water pollution [2]. Methylene blue, an organic dye, has wide variety of applications including temporary hair colorant, paper colouring, dyeing various textile fabrics etc [3]. MB has some serious ill effects on living organisms as it causes nausea, vomiting, diarrhoea, dyspnea, tachycardia, cyanosis, methemoglobin, convulsions etc [4]. MB also has adverse effects on central nervous system as it exerts neurotoxic effects on the central nervous system [5]. In view of these serious harmful effects of dyes, proper treatment is essential before discharging these wastes to environment.

In this direction, a number of methods have been proposed for the removal of these toxic dyes from contaminated water. The said methods include adsorption, reverse osmosis, ion exchange, precipitation, chemical oxidation, and photocatalytic degradation [6]. Among these methods, heterogenous photocatalysis had remained an area of huge interest because of its great potential for the degradation of organic dyes from polluted water. The fabrication of heterocatalyst with a high energy ball mill in absence of any solvent or high temperature has great potential in catalyst fabrication for degradation of organic pollutants from waste water. In semi-conductor photocatalysis, organic dyes are decomposed upon the illumination of light and thus provide an economical, low cost and easy way of water purification from organic pollutants [7]. During semi conductor photocatalysis, electrons get excited from valance band of semi-conductor to conduction band of semi-conductor and as a result electron-hole pairs are created at the surface of photocatalyst. These electron-hole pairs generate reactive oxygen species that oxidise the organic dyes.

Graphene as attracted a great deal of interest of late, owing to its exceptional electronic conductivity, and two dimensional sheet like carbon framework [8]. However, it is still quite challenging to reach the industrial requirements for its large scale production . Additionally, inherent water insolubility of graphene restricts its possible use in number of other application domains [9]. Graphene oxide, being a perfect functionalised graphene, contains numerous reactive surface oxygen functionalities. These reactive oxygen functionalities are mostly present in the form of hydroxyl and epoxy groups on the basal plane and a few as carbonyl and carboxyl at the sheet edge. These functionalities on GO surface provides fresh nucleation sites for the homogenous

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growth of a number of metals, metal oxides, bio molecules, drugs and inorganic particles [10,11]. Thus in comparison with graphene, graphene oxide has attracted huge attention because of its easy availability in bulk quantity, facile chemical functionalization, good water dispersibility and high bio compatibility [8].

Among various semi-conductor photocatalysts, TiO_2 is the most frequently used due to its economical benefits, environmental viability, high thermodynamic stability and strong oxidising power. However, the large band gap of TiO_2 (3.2 eV), its slow reaction rate and very high charge recombination rate has hindered the technology in its practical applications. However, these limitations have been addressed by coupling the metal oxide with noble metal [12], CNTs [13], C_{60} [14] and graphene/ graphene oxide [15,16]. Among these, surface modification of TiO_2 with graphene or graphene oxide are believed to exhibit control on the charge transfer across the TiO_2/graphene oxide interface and thus increase the surface area of the photocatalyst. Literature survey reflects a number of TiO_2/ graphene composites for photodegradation of organic dyes. MB dye degradation have been studied using TiO_2/ graphene composites synthesised via facile one step hydrothermal method [17], hydrothermal hydrolysis of $Ti(SO_4)_2$ [18] and many other related synthetic procedures [19,20].

Different from the above synthetic procedures, we are interested in synthesising the TiO_2/ GO composites via solid phase high energy ball mill, in view of the fact that synthetic procedures are going to affect photocatalytic activity [21,22]. The photodegradation of MB dye over TiO_2/ GO composites synthesised via solid phase high energy ball milling process have not been reported so far. In this work, we report the synthesis of a series of TiO_2/ GO composites via solid phase high energy ball milling using TiO_2 and GO as starting material. The synthesised materials have been characterised by different spectroscopic and surface analysis and have been studied for photocatalytic efficiency of the composite was evaluated against MB dye under UV–Vis light irridation and the synthesised composites showed improved photodegradation of MB dye.

2. Experimental section

The chemicals used in this work were analytical grade and were used as such, i.e. no further purification strategy was employed. The graphite powder, sulphuric acid (H_2SO_4), phosphoric acid, hydrogen peroxide (H_2O_2, 30%), potassium permanganate ($KMnO_4$), titanium tetraisopropoxide, ethanol and acetic acid were few chemicals that were employed to carry out the material synthesis. Distilled deionised water was used as the solvent for the synthesis purposes.

2.1. Synthesis of graphene oxide by improved hammers method.

A reported synthesis procedure was employed for the synthesis of GO [23] although with slight modifications. The natural graphite powder was employed as a precursor. Typically, a 9:1 (v/v) mixture of H_2SO_4 and H_3PO_4 was added to a solid mixture of 0.3 g of graphite powder and 1.8 g of $KMnO_4$. The reaction mixture was then heated to 50 °C and stirred for 12 h for the complete oxidation of graphite. The reaction mixture was allowed to cool to room temperature and poured in about 500 mL of distilled ice cold water. To terminate the oxidation process, 30% H_2O_2 solution was added gradually added. For workup, the centrifugation of filtrate was done and the solid material was washed several times with water, 30% HCl and finally with ethanol. The graphene oxide (GO) thus obtained as dark brown powder was vacuum-dried overnight at room temperature.

2.2. Synthesis of titanium oxide by sol-gel method

TiO_2 nanoparticles were synthesized by an acid assisted sol-gel method using titanium (IV) tetraisopropoxide (TTIP), distilled water and acetic acid as starting materials, following the modified method published in the literature [24].

2.3. Synthesis of TiO_2/GO composites via solid phase ball milling

TiO_2/ GO composites were synthesised by solid phase mechanomixing using high energy ball mill. The composites were synthesised by adding desired amounts of GO and TiO_2 powders into a 80 ml stainless steel grinding jar with zirconium balls (0.85 gm in weight) with a ball to weight ratio of 5:1. The solid mixture was then ball milled at a rotation speed of 400 rpm for a grinding period of 6 hours at room temperature to produce well crystalline and single phase anatase TiO_2/GO composites. For comparision, composites with different weight ratios of TiO_2/GO were also synthesised by same procedure for same grinding time under similar conditions. These samples were labelled as TiO_2-$GO_{0.0}$, TiO_2-$GO_{0.2}$, TiO_2-$GO_{0.3}$, TiO_2-$GO_{0.4}$, TiO_2-$GO_{0.5}$.

2.4. Characterisations

X-ray diffraction (XRD) measurements were performed on a D8-Advanced Bruker-AXS diffractometer by using Cu Kα (λ = 0.1540 nm) as source of x-rays. Fourier transform infrared (FTIR) carried out using a FTIR Analyzer (Nicolet/Avatar 370). The Raman spectras were acquired using laser micro-Raman spectrometer (Renishaw InVia) with an excitation of 532 nm. UV–Vis spectra were performed on the T-80 UV–Vis double beam spectrophotometer. Scanning electron microscopy (SEM) images were collected using field emission scanning electron microscope (JEOL/JSM-6390LV). Transmission electron microscopy (TEM) images were obtained using a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. UV–Vis diffuse reflectance (DR) spectroscopy was employed for optical absorption and emission studies of pure TiO_2 and TiO_2/$GO_{0.4}$ nanocomposite.

2.5. Photocatalytic experiments

Photocatalytic activity of the nanocomposite photocatalyst were confirmed by monitoring the degradation studies of methylene blue (MB) dye as model pollutants from aqueous solution under UV- Vis light irradiation using 500 W mercury-arc lamp. Photocatalytic experiments were carried out under suitable conditions (dark room) with an optimised reaction vessel to light source distance of 15 cm. For the photo measurements, 25 mg of TiO_2/GO nanocomposites was dispersed in 50 ml of aqueous solution containing MB dye of 25 mgL^{-1} initial concentration. Prior to light irridation, the suspensions were magnetically stirred in dark for 30 min to achieve adsorption-desorption equillibrium of MB dye molecules on the photocatalyst surface and was further ensured by absorption studies in dark. The suspension was subsequently subjected to UV- Vis light irradiation under continous stirring. The spectrophotometric analysis of photodegradation process was exercised for the solution aliquot of 3 ml collected at regular intervals. To nullify the scattering effects the catalyst particles were eliminated by carrying out centrifugation at 10000 rpm for 2 min. The variations in the absorption peak maxima in the UV − Vis spectra was directly correlated with the concentration of MB in the supernatant . The photocatalytic activity of nanocomposite photocatalyst were obtained using following formula:

$$\text{Photodegradation of the dye}\,(\%) = (C_o - C_t)/C_o \times 100$$

where C_o is the dye concentration before irradiation and C_t is the concentration of the dye at different irradiation times.

3. Results and discussion

3.1. Phase analysis

XRD analysis was performed to investigate the crystalline structure of the GO based samples. The XRD diffraction patterns of (a) Graphene