



Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis



# Synthesis of nanotitania decorated few-layer graphene for enhanced visible light driven photocatalysis



Reny Thankam Thomas, P. Abdul Rasheed, N. Sandhyarani \*

Nanoscience Research Laboratory, School of Nano Science and Technology, National Institute of Technology, Calicut, Kerala 673 601, India

## ARTICLE INFO

### Article history:

Received 6 February 2014

Accepted 25 April 2014

Available online 2 May 2014

### Keywords:

Graphene

Titania

Nanocomposite

Photocatalytic degradation

Rhodamine B

Photocurrent

Visible light driven photocatalysis

## ABSTRACT

We report a simple method for decorating carboxyl functionalized few-layer graphene with titania ( $\text{TiO}_2$ ) nanoparticles by sonication and stirring under room temperature. The nanocomposites showed a remarkable improvement in visible light driven photocatalysis. From Raman and XRD analysis the number of layers of graphene was found to be 3. The  $\text{TiO}_2$  decorated few-layer graphene (FLG) sheets were characterized by electron microscopy, Raman spectroscopy, infrared spectroscopy, XRD and UV–vis spectroscopy. Titania nanoparticles were uniformly decorated on FLG matrix. The incorporation of titania on FLG enhanced the visible light photocatalytic activity of titania, lowered the electron hole recombination and improved the electron hole mobility. The enhanced life time of the charge carriers was confirmed from the photocurrent measurements. Compared to bare  $\text{TiO}_2$  nanoparticles the FLG– $\text{TiO}_2$  nanocomposites exhibited rapid degradation of Rhodamine B (Rhd B) under solar radiation. It was found that adsorption of dye molecules and the rate of degradation have been greatly enhanced in the FLG decorated with  $\text{TiO}_2$ . The rapid degradation of Rhd B using carboxyl functionalized FLG– $\text{TiO}_2$  within 8 min under solar radiation and 20 min under 30 W UV tube with very low concentration (0.01 wt.%) of the photocatalyst is the highlight of the present report. The mechanism of degradation and charge separation ability of the nanocomposite are also explored.

© 2014 Elsevier Inc. All rights reserved.

## 1. Introduction

Graphene (GR) is considered as one of the significant nanomaterials for the past few years in the field of nanotechnology research. GR being a sheet of  $\text{sp}^2$ -bonded carbon atoms arranged in a honeycomb structure [1] has unique attributes such as the large theoretical specific surface area [2] high surface-to-volume ratio, high electrocatalytic activity, robust mechanical properties and outstanding conductivity which ensure its potential applications in sensors [3–7], energy storage and conversion [8–10], nano-electronics [11–13] super capacitors [14–16] and nanocomposite applications [17–19].  $\text{TiO}_2$  nanoparticles have been well documented as an efficient photocatalyst for various environmental applications [20]. Major limitation of this system is rapid recombination of the charge carriers which can be overcome by incorporating a suitable dopant that delays the recombination process [21]. GR nanocomposite applications include the use of GR in the preparation of highly photoactive composite materials based on titanium oxides [22]. The high surface area and excellent mobility of charge carriers ( $20,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) in GR make it a suitable

candidate for adsorption and degradation of various pollutants. GR is an ideal nanostructured material to be paired with  $\text{TiO}_2$ , increasing its capability to absorb in the visible regime as well as improving its photocatalytic activity.  $\text{TiO}_2$  can interact with graphene oxide sheets through physisorption, electrostatic binding or through charge transfer interactions [23]. The electrons formed upon activation of  $\text{TiO}_2$  are easily transported to GR and recombination of  $\text{e}^-$  and  $\text{h}^+$  is strongly reduced, which increases the process yield. Graphene–titania nanostructures have been studied in the recent years for various applications such as hydrogen evolution through water splitting [24], photocatalytic degradation of various dyes [25]. The route of synthesis mostly adopted for GR– $\text{TiO}_2$  nanocomposite is sol–gel, UV assisted [26], solvothermal [27] or hydrothermal [28].

In the present study, we demonstrate the synthesis of high performance functionalized FLG (FFLG) decorated with  $\text{TiO}_2$  photocatalyst prepared by simple mixing without any calcination or high pressure conditions. GR synthesized in this work is termed as few-layer graphene as per a recent report [29]. FLG when functionalized with carboxyl groups (FFLG) improves the binding of  $\text{TiO}_2$  nanoparticles and enhances the photocatalytic activity. FFLG– $\text{TiO}_2$  showed higher rate of degradation of Rhd B compared to bare  $\text{TiO}_2$  nanoparticles and FLG– $\text{TiO}_2$  (non-functionalized FLG).

\* Corresponding author. Fax: +91 495 2287250.

E-mail address: sandhya@nitc.ac.in (N. Sandhyarani).

Highlight of this photocatalyst system is that it demonstrates complete degradation of the pollutant even at a very low concentration of 0.1 mg/mL under solar irradiation (Intensity  $\sim$ 80,000 luxes) within 8 min which is a remarkable achievement compared to the previous literatures [22] which uses higher amounts of catalyst and high power UV lamps. A possible mechanism of degradation has been proposed through the electron and hole scavenging experiments.

## 2. Experimental

### 2.1. Reagents and materials

Graphite powder (<20  $\mu$ m) and titanium dioxide (15–20 nm) were purchased from Sigma. HCl (35%), Methanol (Himedia), H<sub>2</sub>SO<sub>4</sub> (98% pure), KMnO<sub>4</sub> (99.3%), and H<sub>2</sub>O<sub>2</sub> (30%) were purchased from Merck. NaNO<sub>3</sub> was purchased from Qualigens and methanol was purchased from Himedia. All the chemicals were used as received without further purification. All the experiments were done using ultrapure water with a measured resistivity of 18 M $\Omega$  cm from Millipore (Milli-Q) ultrafiltration system.

### 2.2. Synthesis of graphite oxide (GO)

GO was prepared from graphite powder through modified Hummers method [30–32]. Briefly, 1 g of graphite was added to 23 mL of 98% H<sub>2</sub>SO<sub>4</sub>, followed by overnight stirring at room temperature. Then 100 mg of NaNO<sub>3</sub> was introduced into the mixture and stirred for 30 min. The mixture was kept below 5 °C in an ice bath, and 3 g of KMnO<sub>4</sub> was slowly added into the mixture. After being heated to 35–40 °C, the mixture was stirred for another 30 min. 46 mL of water was then added into the above mixture during a period of 25 min. Finally, 140 mL of water and 10 mL of 30% H<sub>2</sub>O<sub>2</sub> were added into the mixture to stop the reaction. The unexfoliated graphite in this synthesis mixture was removed by repeated centrifugation and filtration (using 5% HCl followed by water) and the final product was dried in vacuum at 65 °C overnight.

### 2.3. Synthesis of FLG from GO

Low temperature exfoliation was used for the conversion of GO to FLG. The GO powder was taken in a crucible and kept at 180 °C for 3 h in a hot air oven. The exfoliation could be visibly confirmed due to the mass change and volume expansion. The mass of FLG after thermal exfoliation was considerably less than graphene oxide. 1 gm of GO powder after thermal exfoliation gives about 700 mg of FLG [33].

### 2.4. Functionalization of FLG

FLG is covalently functionalized through chemical modification with carboxyl groups to change its surface functionality. The FFLG was easily dispersed in water and functionalization also protects FLG from reaggregation [34,35]. FLG was functionalized by treating with nitric acid and sulfuric acid (1:1 v/v) under sonication in a bath sonicator for 2 h at room temperature. The mixture was then washed using deionized water and centrifuged at 1000 rpm for 10–30 min to remove the residual acids in the supernatant. The washing step was repeated until the pH of the supernatant was >6 [36].

### 2.5. Synthesis of TiO<sub>2</sub> decorated FLG

The decoration of TiO<sub>2</sub> nanoparticles on to the FLG matrix was done by simple mixing and sonication. Briefly, FLG and TiO<sub>2</sub>

nanoparticles were taken in a ratio of 1:2 wt.% in 20 mL of milli-Q water. TiO<sub>2</sub> nanoparticles were decorated on to FLG matrix through sonication for 30 min followed by stirring at room temperature for 24 h. The obtained FLG–TiO<sub>2</sub> was then centrifuged at 10,000 rpm for 10 min and washed with water. FFLG was also decorated with TiO<sub>2</sub> nanoparticles referred to as FFLG–TiO<sub>2</sub> under the same conditions. The obtained pellet was dried in oven at 60 °C.

### 2.6. Characterization

The transmission electron microscopy (TEM) images were taken with a Philips CM200 transmission electron microscope operated at 200 kV and scanning electron microscopic (SEM) images were acquired with FE-SEM Hitachi SU6600 Variable Pressure Field Emission. Energy dispersive X-ray analysis (EDX) studies were carried out with FE-SEM for analyzing the elemental composition. The chemical functionalization was studied using Fourier transform infrared (FTIR) (Shimadzu IR Prestige) spectra in the frequency range of 450–4000 cm<sup>-1</sup>. Powder X-ray diffraction (XRD) was performed using Rigaku-smartlab diffractometer with Cu K $\alpha$  operating at 200 kV and 45 mA at a scanning rate of 1° min<sup>-1</sup> (Cu K $\alpha$  radiation  $\lambda$  = 1.5406 Å). Raman spectra were recorded using Thermo-Nicolet 6700 Raman spectrometer. Laser source is Argon ion with 514 nm. The photoluminescence (PL) spectra were obtained by using fluorescence spectrometer (LS 45 Perkin Elmer). The degradation process was monitored with the aid of UV–vis spectrophotometer (UV 1800 Shimadzu). The photocurrent measurements were performed with electrochemical workstation CHI 400A (CH Instruments Texas). The three-electrode system used was indium tin oxide (ITO) covered by a thin film of the samples as working electrode with an active area of 1 cm<sup>2</sup>, Pt wire as auxiliary electrode, and Ag/AgCl (saturated KCl) as reference electrode. The working electrode was prepared by a modified reported procedure [37]. Briefly, ITO electrodes were cleaned by sonicating with acetone and water sequentially. After washing, the electrodes were modified with 100  $\mu$ L of 1 mg/mL samples by drop casting onto the electrode covering the active area and dried under infrared lamp.

### 2.7. Photocatalytic degradation of Rhod B

The photocatalytic degradation of Rhod B dye was monitored by UV–vis absorption spectroscopy. In a typical process,  $5 \times 10^{-6}$  M aqueous solution of the Rhod B and the photocatalysts (TiO<sub>2</sub>, FLG–TiO<sub>2</sub> or FFLG–TiO<sub>2</sub>, 0.1 mg/mL) were placed in a 50 mL beaker. Under ambient conditions and stirring, the vessel was exposed to the UV irradiation produced by two 15 W UV-C tubes with main wave crest at 254 nm. The UV tube was positioned 20 cm away from the reaction vessel. For solar degradation study, the samples were exposed to sunlight (mainly in the summer at UV index >11) with measured light intensity between 77,000 and 85,000 luxes. Light intensity was measured using a Lutron light meter in lux. At regular time intervals 3 mL of the photo reacted solution was withdrawn and analyzed by the variations of the absorption maximum of Rhod B (553 nm) in the UV–vis spectrum.

Dark adsorption test was done to compare the extent of adsorption on TiO<sub>2</sub>, FLG–TiO<sub>2</sub> and FFLG–TiO<sub>2</sub>. In this test, 2 mg of catalyst (TiO<sub>2</sub>/FLG–TiO<sub>2</sub>/FFLG–TiO<sub>2</sub>, 0.1 mg/mL) was dispersed in 20 mL of  $5 \times 10^{-6}$  M Rhod B solution with stirring in dark for 30 min. FLG–TiO<sub>2</sub> and FFLG–TiO<sub>2</sub> contain equal amounts of TiO<sub>2</sub>. Then the dispersion was centrifuged and the UV–vis spectrum of the supernatant was monitored. From the difference in the absorbance before and after adsorption, the amount of dyes adsorbed on the catalyst was estimated.

Download English Version:

<https://daneshyari.com/en/article/607244>

Download Persian Version:

<https://daneshyari.com/article/607244>

[Daneshyari.com](https://daneshyari.com)