Facile synthesis of TiO₂-RGO composite with enhanced performance for the photocatalytic mineralization of organic pollutants
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ABSTRACT

Current research reports the synthesis of reduced graphene oxide (RGO)-TiO₂ nanocomposite by in-situ redox method and graphene oxide by modified hummers method. The ratio of RGO and TiO₂ in the composite was optimized to show best photocatalytic activity for the degradation of targeted pollutants. Optimized (1:10) RGO-TiO₂ nanocomposite was characterized by various techniques viz. X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Brunauer-Emmet-Teller surface area (BET), Raman and diffuse reflectance spectroscopy (DRS) technique confirming successful formation of nanocomposite. XRD results confirm the presence of anatase phase in RGO-TiO₂. Uniform dispersion of TiO₂ nanoparticles on RGO could be seen from TEM images. The obtained results of (1:10) RGO-TiO₂ showed five-fold and two-fold enhancement for the visible light and UV light, respectively, for the photocatalytic mineralization of methylene blue dye as compared to commercial Aeroxide P25 TiO₂. The excellent photocatalytic mineralization activity of (1:10) RGO-TiO₂ could be attributed to the enhanced surface area of composite as well as to its good electron sink capability. (1:10) RGO-TiO₂ could be recycled easily and was found to be equally efficient even after the fourth cycle for the photocatalytic mineralization of methylene blue dye. The non-selectivity of synthesized composite was checked by the mineralization studies of oxalic acid.

Key words | degradation, methylene blue dye, photocatalysis, RGO, TiO₂

INTRODUCTION

Aeroxide P25 TiO₂ is a traditionally and commercially used photocatalyst for environmental remediation due to its supreme properties (Henderson 2011; Nakata & Fujishima 2012; Schneider et al. 2014; Tian et al. 2014; Xu et al. 2014). But still, its use for large scale industrial wastewater treatment is not popular, mainly due to the following impediments such as (i) faster electron-hole recombination rate, (ii) limited response to spectral range as it is active in UV region, comprising just 5% of incident sunlight and (iii) economics involved in separation and reuse of catalyst. Although literature suggests various modifications to the TiO₂ surface by incorporation of metals/non-metals/metal chalcogenides and a variety of carbon materials (Leary & Westwood 2011) to resolve these issues and improve its efficiency but has ended with limited success for scalable applications. To overcome the electron hole recombination problem and to achieve faster electron transport and transfer at interface, composites of TiO₂ with carbon materials such as carbon nanotubes (CNTs), fullerene, activated carbon and graphene have been prepared (Leary & Westwood 2011; Chen et al. 2013). Among these carbon materials, recently, use of graphene is preferred not only due to its high surface area which enables adsorption of hydrophobic organic pollutants to the photocatalyst surface but also due to its exceptional electron sink ability (Bell et al. 2011; Zhao et al. 2012). Graphene is an attractive material for fabricating graphene containing inorganic composites because of its unique electronic properties such as high transparency, a flexible structure and a large theoretical specific surface area (An & Yu 2011; Xiang et al. 2012). Especially, the formation of heterostructures with graphene is viewed as one of the possible ways to extend the technology for large scale application, anticipating its low cost voluminous production in the near future (Kale & Thakur 2015). The composite material is also easy to separate as compared to P25 TiO₂.
Literature reports that different methods to combine graphene oxide (GO) with metal-oxide semiconductor to form stable composites, using hydrothermal method and sol-gel (Wang & Zhang 2011; Zhang et al. 2011; Zhou et al. 2011). Here, we have prepared reduced graphene oxide-TiO$_2$ (RGO-TiO$_2$) composite by altering compositions of precursor of TiO$_2$ and suitably reducing graphene oxide so as to obtain properly tuned RGO-TiO$_2$ composite to rectify more and more limitations of TiO$_2$ as photocatalyst.

**EXPERIMENT**

**Materials**

Graphite powder 99.8% (325 mesh) was purchased from Alfa Aesar. TiCl$_3$ 15% was procured from Sigma-Aldrich. High purity H$_2$SO$_4$, HCl, KMnO$_4$, NaNO$_3$ and H$_2$O$_2$ were purchased from Merck and used as received without further purification. All other reagents were of analytical reagent grade. Deionized (DI) water was used throughout this study.

**Method of preparation of GO**

GO was prepared by chemical oxidation of graphite powder according to the modified Hummer’s method (Mhamane et al. 2012). In this method, 5 g of graphite powder and 3 g of sodium nitrate were mixed in a round bottom flask. To this, 400 mL concentrated H$_2$SO$_4$ was added under constant stirring in an ice bath. Subsequently, 22.5 g of KMnO$_4$ was added to this mixture and was allowed to stir at room temperature for 2 days until brown slurry was obtained. To this slurry, 1 L of 5wt% H$_2$SO$_4$ aqueous solution was added at 98 °C. The final product was purified by acid washing and DI water along with repeating the centrifugation cycle.

**Method of preparation of RGO-TiO$_2$**

Solution A: 22 mg of GO was dissolved in 80 mL of DI water. Solution B: 3 mL of Titanium Trichloride (TiCl$_3$, 15wt%, Sigma-Aldrich) was diluted with 60 mL of HCl solution (1 mL 37wt% HCl, Sigma-Aldrich). Solution A and B were sonicated separately for 20 min and then mixed and sonicated for 10 min. The resulting mixture was stirred for 6 h at 90 °C for the hydrolysis and oxidation of TiCl$_3$. Thus, formed RGO-TiO$_2$ solids were collected by centrifugation, washed several times with DI water and dried in a vacuum oven at 120 °C. The crystallinity was improved by calcinations of the solids in N$_2$ atmosphere at 400 °C for 3 h.

The obtained RGO:TiO$_2$ was in proportion 1:10. In the same way, an appropriate amount of TiCl$_3$ was added to HCl so as to prepare various ratios viz. 1:1, 1:20, 1:50 and 1:100 of RGO:TiO$_2$.

**Characterization**

The crystal structure of GO, P25 TiO$_2$ and RGO-TiO$_2$ composite was determined by powder X-ray diffraction (XRD) analysis (Phillips PW1729, CuK$_\alpha$), the product was sprinkled on pre-greased glass slide and diffractograms were recorded between the angles 10° and 80°. The thermal stability of synthesized materials was characterized by thermogravimetric analysis (TGA; Shimadzu TG-DTG-60H). For TG analysis in a nitrogen atmosphere, parameters used were scanning rate = 1 C/min, and the temperature ranged from 30 to 700 °C. The surface morphology and element distribution of the synthesized composites were analyzed by scanning electron microscope (SEM; JEOL JSM-6360A) attached with energy-dispersive X-ray (EDX) spectroscopy. Raman spectroscopy was performed in confocal micro-Raman spectrometer LabRAM ARAMIS Horiba Jobin-Yvon apparatus with laser excitation wavelength of 532 nm. Transmission electron microscopy (TEM) was done in HR-TEM, FEI Tecnai 300. UV-visible absorbance spectra of the solid materials were recorded between the range of 200 nm and 800 nm using a UV-visible spectrophotometer (JASCO V-670), equipped with a diffuse reflectance sphere and BaSO$_4$ as a reference substance. UV-visible absorbance spectra of the solid were recorded using UV-visible spectrophotometer (Shimadzu 1800 double beam spectrophotometer). The Brunauer-Emmett-Teller (BET) surface area analysis was carried out on a Qquantochrome Autosorb-2 instrument. Chemical oxygen demand (COD) values were measured by standard dichromate method using Spectralab 2015 M COD Digestor and CT-15 COD auto-titrator. Total organic carbon (TOC) analysis was performed using commercially available test kits (NANOCOLOR TOC 60) from Macherey-Nagel, Germany using thermodigester (spectroquant TR 320) and spectrophotometer (NANOCOLOR VIS, Macherey-Nagel).

**Photocatalytic experiment**

The photocatalytic activities of RGO-TiO$_2$ composite photocatalyst and P25 TiO$_2$ were studied for the degradation of methylene blue dye as a targeted pollutant under UV as well as Visible light irradiation. The photocatalytic degradation studies under UV irradiation were carried out in UV photocatalytic reactor consisting of five 8W (254 nm)
UV lamps described in Figure 1. The reactor was surrounded by four UV lamps and the fifth lamp was located axially and held inside the reactor with a quartz jacket. The reactor solution was stirred using a magnetic stirrer for complete circulation of the photocatalyst. Air was bubbled through the reaction solution from the bottom using an aerator with constant speed. Heat generated by the UV lamps was controlled by an exhaust fan. Whereas photocatalytic degradation experiments under visible light irradiation were carried out using a setup for visible light. Here, xenon lamp was used as a visible light source which was collimated in a straight line using a collimator and then passed through visible and IR filters (Edmund optics filters GG400 and KG-3) before it reached the photocatalytic reactor consisting of targeted pollutant solution. Air was bubbled through the reaction solution using an aerator with constant speed and the solution was continuously stirred using stirrer motor. The whole set up is described in Figure 2.

In a typical photocatalytic test performed at room temperature, in case of both UV and visible light irradiation, 20 mg of photocatalyst was added into 50 mL of targeted pollutant aqueous solution of a particular concentration. During the first 10 min of the degradation experiment, the targeted pollutant solution along with the photocatalyst was kept in the dark to achieve adsorption–desorption equilibrium. During irradiation, aliquots were taken out at definite intervals of time and centrifuged at 6,000 rpm and were used to determine the degradation and mineralization of a pollutant by UV-visible spectrophotometry and COD/TOC, respectively.

RESULTS AND DISCUSSION

Characterization of GO and RGO-TiO₂

The oxidation of graphite to GO was confirmed by XRD analysis Figure 3. The presence of a sharp peak at about 2θ = 10.4 corresponds to the (002) reflection of stacked GO sheets. In case of (1:10) RGO-TiO₂, no diffraction peaks of layered GO can be seen, indicating the absence of layer-stacking regularity after reduction by cations. The XRD peaks at about 2θ = 25.4, 37.9, 48, and 54.6 can be indexed to (101), (103,004 and 112), (200), (105 and 211) crystal planes of anatase phase (JCPDS, no. 21–1272). The broad diffraction peaks for (1:10) RGO-TiO₂ indicate small particle size of TiO₂ nanoparticles.

Raman spectroscopy is an important tool for studying structural information of the carbon materials. The Raman spectrum of GO shows the presence of D and G bands Figure 3.
corresponding to peaks at 1,518 cm\(^{-1}\) and 1,580 cm\(^{-1}\), respectively Figure 4. The G band corresponds to sp\(^2\) bonded carbon atoms’ vibration. The D band suggests the presence of sp\(^3\) defects. The intensity of D band is stronger than that of G band indicating the presence of high density of defects and structural disorder in GO. In case of (1:10) RGO-TiO\(_2\) composite, it shows E\(_{1g}\), B\(_{1g}\), A\(_{1g}\) and E\(_g\) bands of TiO\(_2\) corresponding to 158 cm\(^{-1}\), 412 cm\(^{-1}\), 510 cm\(^{-1}\) and 624 cm\(^{-1}\) peaks, respectively, along with D and G bands of GO confirming the formation of stable (1:10) RGO-TiO\(_2\) composite (Yoo et al. 2011).

TGA data show the thermal stability of the composites, Figure 5. The weight loss for GO is due to the presence of substantial oxygen functionalities. The reduced weight loss in case of (1:10) RGO-TiO\(_2\) clearly depicts the binding and successful functionalization of RGO with TiO\(_2\) nanoparticles (Zhang et al. 2010; Shen et al. 2011).

From the solid UV absorbance spectra as shown in Figure 6, increase in the absorption of light by (1:10) RGO-TiO\(_2\) composite may be ascribed to the dark color of the composite. Also, it is concluded that there is no change in the band gap of the composite by the addition of GO to the composite (Nainani et al. 2012).

The TEM image of the chemically exfoliated GO sheet is shown in Figure 7(a). The presence of wrinkles and folds on the sheet is the characteristic feature of a few-layered GO sheet. The TEM image of (1:10) RGO-TiO\(_2\) as shown in Figure 7(c) displays uniformly dispersed spherical morphology of anatase TiO\(_2\) nanoparticles on RGO sheets. The TiO\(_2\) nanoparticles are well separated from each other which shows that aggregation was well prevented. The average particle size of TiO\(_2\) nanoparticles was found to be 10 nm. The inset shows SAED pattern of (1:10) RGO-TiO\(_2\) confirming the crystalline nature of graphene with the presence of a six-sided shell, i.e. honeycomb lattice of graphene. The HRTEM image Figure 7(d) of (1:10) RGO-TiO\(_2\) clearly shows the lattice fringes of TiO\(_2\) nanoparticles are parallel to RGO sheets. The lattice spacing of TiO\(_2\) was measured to be 0.35 nm, which corresponds to the (101) plane of anatase TiO\(_2\) (JCPDS no. 21–1272).

Energy dispersive X-ray spectroscopy (EDS) analysis shows the elemental composition of (1:10) RGO-TiO\(_2\) composite as shown in Figure 8. The composition shows 72% of titanium, 19% of oxygen and 9% of carbon. The elemental composition of (1:10) RGO-TiO\(_2\) matches with ratio 1 as 10.

BET surface area of the (1:10) RGO-TiO\(_2\) composite was found to be high, i.e. 161 m\(^2\)/g as compared to P25 TiO\(_2\).
having a surface area of 50 m²/g (Table 1). The high surface area, that is availability of active sites for the reaction, is a beneficial factor for enhancement of photocatalytic activity of (1:10) RGO-TiO₂ composite (Neppolian et al. 2013).

Application and optimization of RGO-TiO₂ for photocatalytic degradation of methylene blue dye

The RGO-TiO₂ composites of different proportions that were prepared were analyzed for the photocatalytic degradation of methylene blue dye of 5 × 10⁻⁴ M initial concentration (Figure 9).

It was observed that even after 40 min of UV irradiation of the (5 × 10⁻⁴ M) methylene blue dye there is negligible photolysis without a catalyst. Thus, the dye is stable under UV light irradiation as can be seen from Figure 9. The order of the photocatalytic degradation efficiency of methylene blue dye under UV light exposure was found to be as follows: (1:10) RGO-TiO₂ > (1:20) RGO-TiO₂ > (1:50) RGO-TiO₂ > (1:100) RGO-TiO₂ > TiO₂ > (1:1) RGO-TiO₂, obtained results suggest that the (1:10) RGO-TiO₂ is a better nanocomposite photocatalyst for efficient photocatalytic degradation of methylene blue dye. In photocatalysis, when light is absorbed by the photocatalyst there is formation of charged species, i.e. electron and...
hole. RGO mainly acts as a charge carrier to prevent electron hole recombination or to prolong the time of recombination, thus increasing photocatalytic yield.

At the lower concentration of RGO, i.e. in case of (1:100), (1:50) and (1:20) RGO-TiO$_2$ the proportion of RGO is too low compared to TiO$_2$, to prevent electron hole recombination resulting in poor photocatalytic activity as compared to that of the (1:10) RGO-TiO$_2$ sample. On the other hand, excess of RGO in the system results in scattering and absorbance of photons by carbon in RGO, thus shielding the TiO$_2$ leading to decrease in photocatalytic activity as is evident from the results of (1:1) RGO-TiO$_2$ as shown in Figure 9.

Thus, it is concluded that optimization of RGO-TiO$_2$ ratio is crucial parameter for the nanocomposite to show synergistic effect and best photocatalytic activity. Hence, for further photocatalytic studies (1:10) RGO-TiO$_2$ sample was used as the standard optimized photocatalyst. This optimized (1:10) RGO-TiO$_2$ composite was further tested for its photocatalytic activity under visible light irradiation.

Table 1 | BET surface area of the catalyst used

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<tr>
<th>Photocatalysts</th>
<th>Surface area (m$^2$/g)</th>
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<tr>
<td>Aerioxide P25 TiO$_2$</td>
<td>50*</td>
</tr>
<tr>
<td>(1:10) RGO-TiO$_2$</td>
<td>161</td>
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*Information supplied by manufacturer.
For confirming adsorptive role of the dye on the photocatalyst, the same experiments were performed in the dark using the same dose and initial concentration of the dye for the same irradiation period of 50 min. From Figure 10, it can be concluded that there is negligible adsorption of methylene blue dye on the surface of the photocatalyst.

**Photocatalytic degradation of methylene blue dye in UV light and visible light**

Figure 11 shows time dependent degradation plot for methylene blue dye. There was complete degradation of methylene blue dye within 20 min only in the cases of both (1:10) RGO-TiO$_2$ and P25 TiO$_2$. The same experiments were carried out under visible light irradiation (see Figure 12). The obtained results show a similar kind of degradation pattern as observed under UV light irradiation, highlighting the excellent photocatalytic activity of RGO-TiO$_2$ composite in UV as well as visible light.

Percent reduction in TOC, as shown in Figure 13, is a direct measure of mineralization of methylene blue dye. The obtained TOC results showed the improved mineralization capability of (1:10) RGO-TiO$_2$ (64%) compared to P25 TiO$_2$ (27%). Interestingly, it is observed that although P25 TiO$_2$ showed complete degradation of methylene blue dye as observed by UV-visible spectrophotometric data, i.e. Figure 11 showed only 27% mineralization of methylene blue dye as obtained from TOC data. Although composite and P25 TiO$_2$ shows comparable photocatalytic degradation activity, the photocatalytic mineralization activity results of (1:10) RGO-TiO$_2$ composite is two times higher than P25 TiO$_2$. Also, from the visible light photocatalysis results the percent reduction in TOC as shown in Figure 14 showed improved mineralization activity of (1:10) RGO-TiO$_2$ (46%) compared to P25 TiO$_2$ (9%) after two hours. The enhanced photocatalytic mineralization of dye by (1:10) RGO-TiO$_2$ compared to P25 TiO$_2$ can be attributed to the availability of the high surface of catalyst as well as the suppression of electron hole recombination, as RGO acts as a good electron sink (Zhou et al. 2011). The above results clearly indicate the substantial
mineralization capability of synthesized composite photocatalysts compared to traditional P25 TiO2. Further, the non-selectivity of synthesized composite photocatalyst was confirmed from the value of 70% TOC reduction of oxalic acid by (1:10) RGO-TiO2 composite after 1 h under UV light irradiation.

Recycling and reuse of the photocatalyst

For investigating the photocatalytic stability of (1:10) RGO-TiO2 nanocomposite under UV light irradiation, recycling experiments were carried out using optimized composite (1:10) RGO-TiO2 nanocomposite. For each new cycle, the photocatalyst was allowed to settle naturally for 2 h and vacuum-dried at 100 °C for a couple of hours. As shown in Figure 15, it can be observed that the percentage reduction in COD of methylene blue after 1 h is nearly constant without loss of activity of (1:10) RGO-TiO2 nanocomposite.

Also from the IR data (see Figure 16), it is confirmed that there is no sign of adsorption of organic molecules and poisoning of catalyst by any structural change in the photocatalyst before and after reaction. Thus, it is confirmed that (1:10) RGO-TiO2 nanocomposites have a high stability for repetitive use. The recycling of (1:10) RGO-TiO2 is found to be much easier than compared to P 25 TiO2, where the later remain suspended in the solution for days together. The easy recycling of composite is evident from the carbon form in (1:10) RGO-TiO2.

In the case of real wastewater systems, the mineralization of pollutants is of utmost importance. Hence, the synthesized composite could be seen as a potential photocatalyst as far as real industrial effluent is concerned.

Probable mechanism

During photocatalysis, adsorption of pollutant molecules on the surface of photocatalyst and the charge transportation and separation are crucial factors. A probable mechanism for photodegradation of pollutants by TiO2-RGO composite is illustrated in Figure 17. The conduction band (CB) minimum and valence band (VB) maximum of TiO2 are located at −4.29 eV and −7.41 eV (vs. vacuum) (Mitin
et al. 2012), respectively, and the work function of graphene is -4.42 eV (Garg et al. 2014) (vs. vacuum). When UV light strikes the surface of the composite photocatalyst there is a generation of electrons in the VB and holes in CB of TiO₂. Due to the presence of a large amount of oxygen sites that are able to accept photoinduced electrons from TiO₂ (Zhang et al. 2011; Wang & Zhang 2011; Zhou et al. 2011) and due to the favorable positions of CB minimum of TiO₂ and work function (WF) of RGO, there is an efficient interfacial transfer of electrons from TiO₂ to RGO. Further, the concentration of pollutants near the RGO surface is increased due to the increased adsorption of pollutant molecules as the BET surface of the composite photocatalyst is three times higher than P25 TiO₂. Consequently, pollutant molecules, after getting adsorbed on the graphene surface, then get transferred to the residual vacancies on TiO₂ surface due to slip-induced surface diffusion where they get oxidized by the holes directly or by the photoactive radicals generated in the photocatalytic reactions to finally get mineralized into CO₂, H₂O and mineral acids (Kale & Thakur 2015). Although P25 TiO₂ and RGO-TiO₂ show a similar kind of photocatalytic degradation of methylene blue dye, it is not able to degrade the intermediates formed during the process while RGO-TiO₂ is able to degrade the different intermediates formed during the process, as evident from TOC and COD data.

In summary, the overall synergistic effect of RGO as an adsorbent and electron sink results in the enhanced visible light mineralization of pollutant molecules on (1:10) RGO-TiO₂ composite surface as compared to P25 TiO₂.

CONCLUSIONS

In this study, we present the synthesis and characterization of RGO-TiO₂ nanocomposites derived from in situ preparation and GO via a redox reaction. The influence of RGO on the photocatalytic activity of (1:10) RGO-TiO₂ nanocomposites has been examined systematically by considering different weight addition ratios of graphene. (1:10) RGO-TiO₂ was found to be the best ratio for the maximum mineralization of methylene blue dye. The results showed that the (1:10) RGO-TiO₂ nanocomposites possess excellent structure and great electrical and optical properties. XRD results showed the formation of anatase phase in (1:10) RGO-TiO₂. TGA results revealed the high stability of (1:10) RGO-TiO₂ nanocomposite. (1:10) RGO-TiO₂ possesses a high surface area of 161 m²/g. DRS of (1:10) RGO-TiO₂ composite showed an increase in absorption range of light and no change in band gap. TEM results showed uniform deposition of TiO₂ nanoparticles on RGO sheets. Raman spectrum of composite depicts the formation of characteristics of D band at 1,318 cm⁻¹ and G band at 1,580 cm⁻¹ for RGO sheets. The photocatalytic degradation of methylene blue dye as observed from the UV-visible spectrophotometric data indicates a similar degradation pattern for both RGO-TiO₂ and P25 TiO₂ in UV as well as visible light. However, there were two-fold and five-fold increases in photocatalytic mineralization activity (as evident from TOC data) of (1:10) RGO-TiO₂ under UV and visible light irradiation, respectively. This enhancement may be
attributed to the excellent electron sink capacity of RGO and to the high surface area of composite catalyst over P25 TiO2. The non-selectivity of as synthesized composite photocatalyst was confirmed by substantial mineralization of oxalic acid. The (1:10) RGO-TiO2 composite photocatalyst was found to be very easily separable from the aqueous medium as compared to P25 TiO2. The composite catalyst was reused four times without any loss of photocatalytic mineralization activity. The (1:10) RGO-TiO2 was found to possess good potential for the photocatalytic mineralization of pollutants along with excellent recycle and reuse capability.

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REFERENCES


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