# Effect of Reduced Graphene Oxide and Annealing Temperature on the Photocatalytic Properties of Titanium Oxide

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**Abstract:** Photocatalytic performance of titanium oxide (TiO<sub>2</sub>) was boost up by preparing TiO<sub>2</sub>/ reduced graphene oxide (TiO<sub>2</sub>/ GR) composites using sol–gel method. These composites were characterized by X-ray diffraction, Raman and UV-Visible spectroscopy. The photocatalytic activity of photocatalyst was examined by the recording the degradation of methyl orange (MO) dye under UV irradiation. It was found that degradation was 1.67 times faster for TiO<sub>2</sub>/ GR (200mg) catalyst as compared to pure TiO<sub>2</sub>. The photocatalytic activities of different phases of TiO<sub>2</sub> were also studied and results revealed that the degradation was faster in anatase phase of TiO<sub>2</sub> as compared to rutile phase. UV–Visible spectra showed that the increase in catalyst loading raise the degradation of MO up to a certain limit.

Key words: Photocatalysis, Sol-Gel, TiO<sub>2</sub>/ GR composite, UV-Visible spectroscopy, X-ray diffraction.

## 1. Introduction

Rapid growth of industries in the world has increase the pollutants in the water such as heavy metals in ground water [1], various types of dyes [2], inorganic & organic waste materials. Among these pollutants, dyes are harmful and difficult to remove because of aromatic and heterocyclic structures. These types of wastes decrease the oxygen level in water (< 6ppm) and hence prove very harmful for aquatic animals and plants. Different physical, biological and chemical conventional methods [3]-[5] are inefficient to remove dyes from water. Currently, adsorption using adsorbants has become interesting method for the removal of dyes from water because of its low cost and high efficiency. Lots of work have been carried out using metal oxides such as Titanium dioxide (TiO<sub>2</sub>) [6], [7], Zirconium oxide (ZrO<sub>2</sub>) [8], Iron oxide [6]-[9] and ZnO [10] due to their photocatalytic properties. Among these, TiO<sub>2</sub> as adsorbents is best due to its non-toxicity, strong oxidizing and reducing power [11], stability, water insolubility [12], [13] and most importantly semiconductor behavior [14], [15].

Different methods have been used to improve photocatalytic properties of  $TiO_2$  including ion doping for the degradation of 4-nitrophenol [16], adding a coadsorbent such as  $ZrO_2$  to increase the adsorption efficiency [8],  $TiO_2$ / carbon nanotube composite [14], [17], [18], magnetic  $TiO_2$ / graphene composite for removal of herbicides [14], [19],  $TiO_2$ / CuO<sub>2</sub> composite to eliminate color from water [20] etc. As per

literature, work on dye removal from water using  $TiO_2$ / graphene composite synthesized by sol gel technique has been still in progress. Looking at these observations and focusing on graphene based materials [21], the present work is directed towards the removal of methyl orange (MO) dye from water using a coadsorbent.

 $TiO_2$  exists in anatase and rutile phase. Anatase phase possess more photocatalytic activity [15] due to its bandgap ( $E_{g anatase} > E_{g rutile}$ ). But its applications in dye removal at large scale are limited because of quick recombination of electron hole pair and low absorption of UV light. So, a suitable adsorbent which help in absorption of light is required to enhance its photocatalytic properties. Graphene is suitable for this purpose due to its large specific surface area, good electrical and optical properties [22], [23]. It acts as a promoter in photocatalytic reaction by capturing the electron in between the reaction so that electron hole pair recombination can be minimized [24]. Thus, graphene not only support the TiO<sub>2</sub> nanoparticles but also help in absorption of light due to its larger surface area [25], [26]. In previous work, we studied the effect of graphene in enhancing photocatalytic properties of  $ZrO_2$  [21]. The work has been extended to TiO<sub>2</sub> nanoparticles due to its small band gap and good photocatalytic activity towards light compared to  $ZrO_2$ .

In the present work,  $TiO_2/$  reduced graphene oxide ( $TiO_2/$  GR) catalysts prepared by sol-gel method were used for the study of its photocatalytic activity for removal of MO dye in the presence UV light by increasing absorption of light and decreasing electron hole recombination.

#### 2. Experimental

#### 2.1. Materials

Graphite powder (purity 99.99%), sodium nitrate (99.0%), sulphuric acid, potassium permanganate (99%), hydrogen peroxide and hydrochloric acid were purchased from Rankem RFCL Pvt. Ltd., India. Titanium tetra isopropoxide (TTIP) was obtained from Sigma Aldrich. Ethanol, MO was purchased from s-d fine- chem. Limited Mumbai, India.

#### 2.2. Synthesis of Graphene Oxide

Graphene oxide (GO) was synthesized by Hummers method. Graphite (2 g), NaNO<sub>3</sub> (1 g) were mixed in cooled concentrated sulphuric acid (46 ml) under stirring in ice bath. KMnO<sub>4</sub> (6 g) was gradually added to the above placed mixture with stirring and cooling so that the temperature of mixture was maintained between  $10-15^{\circ}$ C [19], [21]. The reaction mixture was then stirred at 40°C for 30 minutes. Subsequently, 80 ml of high purity water added to the formed paste, followed by another 90 minutes stirring at 90°C. Successively, to stop the oxidation reaction additional 200 ml water was added. 6 ml of 30% H<sub>2</sub>O<sub>2</sub> was added in above mixture sequentially to destroy the excess KMnO<sub>4</sub>. The complete removal of KMnO<sub>4</sub> was indicated by color change in to yellow. Sometimes color of the solution was yellow before addition of H<sub>2</sub>O<sub>2</sub> which indicated complete reduction of KMnO<sub>4</sub>. The solution was then washed with HCl (10%) to remove sulphate. Subsequently it was filtered and washed several times with DI water. The filtered paste was dissolved in 100 ml DI water. The solution was ultrasonicated for 1 hour and centrifuged for 20 minutes at 4000rpm. GO powder thus obtained was collected and dried at room temperature.

#### 2.3. Synthesis of TiO<sub>2</sub>

TiO<sub>2</sub> nanoparticles have been synthesized from TTIP using sol gel method. TTIP (16 ml) was mixed with ethanol (27.6 ml) and acetic acid (318  $\mu$ l) and continuously stirred for 1½ hours at 90°C in dark environment. The obtained sol was clear, homogenous with yellowish appearance and was kept for 24 hours in dark. After that it was dried in oven at 100°C for one day. The obtained TiO<sub>2</sub> powder was annealed at 500°C, 800°C named as T<sub>5</sub> and T<sub>8</sub> respectively.

# 2.4. Synthesis of TiO<sub>2</sub>/ GR Catalyst

The TiO<sub>2</sub> and GO act as a starting material for synthesis of TiO<sub>2</sub>/ GR composite. T<sub>5</sub> (1.08 g, 0.135 mol) was dispersed in ethanol (100 ml) and GO (100 mg) was dispersed in DI water (10 ml) by sonication for 1hour respectively. Subsequently, both solutions were mixed and refluxed for 36 hours by addition of 0.1 ml of hydrazine hydrate and HCl. HCl modifies the surface of TiO<sub>2</sub> so that they get attached to GO sheet. Further, GO get reduced to GR by hydrazine hydrate (act as reducing agent for GO). The resulting nanocomposite (T<sub>5a</sub>) were collected by centrifuge and dried in oven at 60°C overnight.

Similar method was used to prepare other  $TiO_2/GR$  ( $T_{5b}$  and  $T_{5c}$ ) catalyst by fixing the amount of  $TiO_2$  and using 133mg and 200mg of GO respectively. Similarly  $TiO_2/GR$  composite prepared from  $T_8$  are named as  $T_{8a}$ ,  $T_{8b}$ ,  $T_{8c}$  having 100mg, 133mg and 200mg GO respectively.

#### 2.5. Experimental Procedure for Degradation Studies:

A 500 ml solution of MO (4 mg) was prepared in water and 1ppm of  $H_2O_2$  was added into it to remove extra electron generated during reaction.  $T_5$  (30 mg) was added to the 100 ml of the solution of MO. The reaction temperature was maintained at room temperature for all the experimental trials. The solution was kept under UV wavelength and small amount of solution was withdrawn from the reaction mixture at regular intervals and analyzed using UV spectrophotometer. The experiment was repeated with other TiO<sub>2</sub> and TiO<sub>2</sub>/ GR samples and also, by adding varying amount (30 mg, 50 mg, 100 mg and 150 mg) in the solution of MO.

#### 3. Results and Discussions

The crystal structure of the resulting products were characterized by X-ray power diffraction (XPERT-PRO diffractometer (45 kV, 40 mA) equipped with a Giono-meter PW3050/60 working with Cu K<sub> $\alpha$ </sub> radiation of wavelength 1.5406Å in the 2 $\theta$  range from 5 to 80°). The band gap of prepared samples and the changes in the concentrations of MO in the aqueous solution were examined by absorption spectra measured on a UV–Vis absorption spectrophotometer (UV–Vis) (Perkin Elmer, Lamba 650). Raman spectra were recorded with a Raman microscope (Renishaw inVia), using a 514 nm wavelength laser having 50% power with 2400 l/ mm grating focused through an inverted microscope (Leica), via a 20x objective.

## 3.1. Characterization

## 3.1.1. XRD analysis



Fig. 1. XRD pattern of GO synthesized using Hummer's method

Fig. 1 represents the XRD of graphite, GO and reduced GO. Diffraction peak of graphite observed at  $2\theta=26.4^{\circ}$  could no longer be detected in GO. While the XRD pattern for GO exhibited a strong and sharp peak at  $2\theta=10.56^{\circ}$  corresponding to the (002) indicates that a highly oxidized GO sample has been synthesized. Interlayer distance of GO (8.37Å) was greater than graphite (3.36Å). The larger interlayer distance of GO might be due to the formation of oxygen-containing functional groups such as hydroxyl, epoxy and carboxyl in graphite. In XRD pattern of GR the peak corresponding to GO at  $2\theta=10.56^{\circ}$  is completely disappeared. This can be ascribed to the removal of functional groups and may indicate complete deoxygenation of GO and exfoliation of GR.

Fig. 2 (a, b) depicts the XRD pattern of  $T_5$ ,  $T_8$  and their TiO<sub>2</sub>/ GR composites ( $T_{5a}$ ,  $T_{5b}$ ,  $T_{5c}$ ,  $T_{8a}$ ,  $T_{8b}$  and  $T_{8c}$ ) obtained by sol-gel route respectively. The synthesized  $T_5$  nanoparticles showed crystalline nature with 20 peaks lying at 25.2°(101), 37.7°(004), 48°(200), 55°(105) corresponding to anatase phase and peak at 54°(211) for rutile phase respectively.

 $T_8$  nanoparticles displayed peaks at 27.47° (110), 36.09° (101), 41.31° (111), 54.41° (211), 56.64° (220) and 69.41° (301) corresponding to rutile phase. The XRD data confirms that TiO<sub>2</sub> have anatase phase at 500°C and rutile at 800°C [14]. Morever, GO peak disappeared in pattern of TiO<sub>2</sub>/ GR composites (Fig. 2a, b), revealing that GO was reduced by hydrazine hydrate during the reaction. Also, the peak corresponding to that of graphite was absent in the composites, indicating the decoration of TiO<sub>2</sub> onto graphene sheets which cause the enlargement and disorder in the layer of graphene. In addition, it is observed that GO in TiO<sub>2</sub> does not affect the phase of the particles of the composites.



Fig. 2. Phase analysis of (a) TiO<sub>2</sub> annealed at 500°C (T<sub>5</sub>) and TiO<sub>2</sub>/ GR composite (T<sub>5a</sub>, T<sub>5b</sub> and T<sub>5c</sub>) of different concentration showing anatase phase is dominate over rutile phase, (b) TiO<sub>2</sub> annealed at 800 °C (T<sub>8</sub>) and TiO<sub>2</sub>/ GR composite (T<sub>8a</sub>, T<sub>8b</sub> and T<sub>8c</sub>) of different concentration showing rutile phase is dominate over anatase phase

The powder size was calculated by using Debey Scherrer's formula

#### $D=K\lambda/(\beta cos\theta)$

where D is the crystal size;  $\lambda$  is the wavelength of the X-ray radiation ( $\lambda$ =0.15406 nm) for CuK $\alpha$ ; K is usually taken as 0.89;  $\beta$  is the line width at half-maximum height and  $\theta$  is the Bragg angle [27]. The average value of

crystallite size obtained using this formula is 7.01 nm and 37.3 nm for  $T_5$  and  $T_8$ , respectively.

## 3.1.2. Raman analysis

The Raman spectrum (Fig. 3) of  $T_8$  indicates the presence of crystalline nanoparticles and showed Raman bands at 435(E<sub>g</sub>) and 600(A<sub>1g</sub>) for the rutile structure [28] which is in good agreement with the reported XRD pattern. In addition to different TiO<sub>2</sub> modes, the broad D-band (defect-induced mode) at 1379 cm<sup>-1</sup> and G band (E<sub>2g</sub> graphite mode) at 1596 cm<sup>-1</sup> were observed in T<sub>8b</sub> composites shown in Fig. 3.



Fig. 3. Raman spectra of  $T_8$  and  $T_{8b}$  showing peaks corresponding to rutile phase of TiO<sub>2</sub>

As position of  $E_g$  and  $A_{1g}$  Raman bands does not changed by the addition of GR confirming that GR addition does not affect the phase of TiO<sub>2</sub>.

## 3.1.3. UV-Visible analysis

## **Band gap calculation**

The band gap is a crucible parameter to understand the photocatalytic properties of material. The band gap can be estimated from UV-Visible spectra. In order to investigate change in the band gap of  $TiO_2$  with the addition of GR the UV -Visible absorption spectra of  $T_8$  and  $T_{8c}$  composite was recorded. Tauc plots of  $T_8$  and  $T_{8c}$  are shown in Fig. 4, the band gap is calculated using Tauc's expression [29]:

$$\alpha h \nu = A (h \nu - E_g)^n$$

where  $\alpha$  is absorption coefficient, A is a constant which is almost independent of the chemical composition of the semiconductor, hv is the photon energy and E<sub>g</sub> is the optical band gap, n is 2 for an indirect transition and  $\frac{1}{2}$  for a direct transition.

The band gap ( $E_g$ ) of TiO<sub>2</sub> can be estimated from the plot of  $(\alpha h\nu)^2$  versus photon energy ( $h\nu$ ) shown in Fig. 4. The extrapolated intercept correspond to the band gap energy at 2.98eV for T<sub>8</sub> and 3.23eV for T<sub>8c</sub>. The band gap ( $E_g$ ) estimated for T<sub>8</sub> (2.98eV) is in close agreement with the reported value for rutile

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nanostructures (3.0–3.1eV). With the addition of GR in  $T_8$ , the band gap increases to 3.23eV resulting in the improvement of degradation of MO due to reduced chances of electron hole pair recombination.



Fig. 4. Tauc Plot  $(\alpha h\nu)^2$  Versus Photon Energy  $(h\nu)$  of the Synthesized (a) T<sub>8</sub> and (b) T<sub>8c</sub>.

#### 4. Photo Catalytic Analysis

Photocatalytic process involves acceleration of the reaction in the presence of catalyst (such as  $TiO_2$ ) when photon of energy greater than band gap of catalyst falls on it. The photoexcited electrons react with oxygen molecule to form super oxide anion ( $O_2$ -) and positive hole breaks apart the water molecule to form hydrogen gas and hydroxyl radical (OH\*).

The degradation of MO dye using pure and GR doped  $TiO_2$  (annealed at 500°C and 800°C) was compared by photo catalysis process using UV light. Fig. 5(a) shows the absorbance of MO with time under irradiation of UV light using pure  $TiO_2$  (annealed at 500°C) as photocatalyst. The absorption peak diminishes with increasing irradiation time of UV light indicates the degradation of MO as  $TiO_2$  absorb more energy from UV light for long exposure time.

#### 4.1. Effect of Catalyst Loading

In order to determine the effect of catalysts ( $TiO_2$  and  $TiO_2/GR$ ) on the degradation of MO the experiments were carried out with and without catalyst loadings.

# 4.1.1. Effect of TiO<sub>2</sub>

Effect of  $TiO_2$  as catalyst can be easily seen on the degradation of MO, as MO remains unaffected in the absence of catalyst. In our experiments, amount of photo catalyst varies from 30 to 150 mg/ 100 ml of the dye solution. More interestingly degradation first increases (up to 100 mg catalyst loading of  $T_5$  and 50 mg catalyst loading for  $T_8$ ) and then decreases for further increase in amount of catalyst. This may be due to decrease in light penetration through the solution with increasing dose. Moreover, higher amount of catalyst increase the turbidity of the solution. Fig. 5 shows the variation of absorption with time and amount of  $TiO_2$  catalyst loading for  $T_5$ .

#### **4.1.2 Effect of annealing temperature**

From Table 1 it is clear that the photo degradation of MO was more for  $T_5$  as compared to that for  $T_8$ . The difference in photocatalytic activity was due to particle size and phase. Small crystalline size gives high surface area and hence provides more sites for the adsorption of reactive species. As  $T_5$  has smaller crystalline size and exists in anatase phase which is more photoactive than  $T_8$  having larger crystalline size which exist in rutile phase (cleared from XRD) [15].

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Concentration (mg)	Degradation time (minutes)					
	$TiO_2$ annealed at 500°C				$TiO_2$ annealed at 800°C	
	$T_5$	T <sub>5a</sub>	T <sub>5b</sub>	T <sub>5c</sub>	$T_8$	T <sub>8c</sub>
30	73	56	50	48	90	75
50	54	53	48	44	72	68
100	46	32	38	30	85	80
150	50	37	42	40	100	86

Table 1. Degradation Time of  $TiO_2$  (Annealed at 500°C and 800°C) and  $TiO_2$ / GR Composites

# 4.1.3. Effect of GR

Furthermore, the effect of GR was studied in the degradation of MO by preparing  $TiO_2$ / GR composites. The photocatalytic activities of  $TiO_2$  was enhanced by addition of GR, as when UV light falls on  $TiO_2$  the generated electron were transferred to graphene and the recombination of photo-generated electron-hole pairs was reduced. The amount of graphene is important parameter in determining the photocatalytic activity of  $TiO_2$ / GR composites. Fig. 5 b, c, d show the absorbance spectra of MO with time, under irradiation of UV light using  $T_{5a}$ ,  $T_{5b}$  and  $T_{5c}$  as photo catalyst.



Fig. 5. UV-Visible absorption spectra of degradation of MO with T<sub>5</sub>, T<sub>5a</sub>, T<sub>5b</sub> and T<sub>5c</sub> w.r.t. time and different amount of catalyst loading (30mg, 50mg, 100mg and 150mg)

It has been concluded that the addition of GR enhance the photocatalytic activities of  $TiO_2$  as it enhances the light absorption due to its higher surface area and promote electron-hole separation [27] during

reaction. Also with increasing amount of GR in  $TiO_2$  the degradation of MO occur faster (Table 1 and Fig. 5b, 5c and 5d) as degradation time was minimum (30 minutes) for  $T_{5c}$  having greater amount of GR. Similar effect was also observed in  $T_{8a}$ ,  $T_{8b}$  and  $T_{8c}$  (degradation time for  $T_{8c}$  shown in Table 1) although there is small effect of GR in this case due to rutile phase of  $TiO_2$  at 800°C which does not have good photocatalytic properties like anatase phase, as it requires 68 min and 80 min for degradation of MO using  $T_{8c}$  as compared to much lesser time of 44 min and 30 min using  $T_{5c}$  using 50 mg and 100 mg of catalyst loading respectively.

Degradation constant (DC) for reaction at any time can be calculated by equation

$$\% DC = \frac{C_{initial} - C_{final}}{C_{initial}} * 100$$

where  $C_{initial}$  is the initial concentration and  $C_{final}$  is the concentration of MO at any time.

The degradation curve of pure and GR doped  $TiO_2$  annealed at different temperature are shown in Fig. 6, 7. It can be observed that degradation is more in  $T_5$  (74.2% for 50mg) shown in Fig. 6a as compared to  $T_8$ (66.6% for 50mg) shown in Fig. 7(a). With increasing GR doping in  $TiO_2$  degradation also increases up to 80.25% for 50mg and further it increase to 88.25% with 100mg of  $T_{5c}$  catalyst loading (Fig. 6d) in MO solution. Fig. 8 shows decolorization of MO dyes is in the presence of 100mg  $T_{5a}$  catalyst in 0, 10, 15, 20, 25, 30, 32 min.



Fig. 6. % Degradation constant curve of TiO<sub>2</sub> annealed at 500°C (T<sub>5</sub>) and TiO<sub>2</sub>/ GR composite (T<sub>5a</sub>, T<sub>5b</sub> and T<sub>5c</sub>) for different concentration in MO solution



Fig. 7. % Degradation constant curve of TiO<sub>2</sub> annealed at 800°C ( $T_8$ ) and TiO<sub>2</sub>/ GR ( $T_{8c}$ ) composite



Fig. 8. Decolourization of MO solution containing T<sub>5a</sub> (100mg) in 0, 10, 15, 20, 25, 30, 32 min.

# 5. Conclusion

The TiO<sub>2</sub>/ GR composites were successfully prepared using sol gel method and were used to degrade MO from the solution. The rate of photo decolorization increases with increase in catalyst dose up to an optimum loading after which degradation of MO decreases as higher concentration act as a barrier to transferred UV light in the solution. The degradation time as well as degradation rate increases with increase in the concentration of GR in TiO<sub>2</sub> in the solution. This may be due to that GR efficiently separate out the electron hole pair by capturing the electron during reaction. In this work, degradation of MO was increased to 88.25% in 30 min with addition of GR as compared to pure TiO<sub>2</sub> which degraded to 81.25% in 46 min.

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