Effect of Graphene in Enhancing the Photo Catalytic Activity of Zirconium Oxide

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Abstract Graphene, have two-dimensional structure with high conductivity, extremely high specific surface area and superior electron mobility etc. It has been regarded as an important synthesis material for various composite materials used in many applications. Especially, graphene-based semiconductor photo catalysts have attracted extensive attention because of their usefulness in environmental applications such as air cleanup, water disinfection, hazardous waste remediation, and water purification. The present study involves the photo catalytic degradation of methyl orange by photo catalytic process using different concentrations of ZrO₂/graphene synthesized at different annealing temperature. A series of zirconium oxide (ZrO₂, zirconia) and graphene (Gr) composites with different contents of Gr (5.7, 7.3, 8.3 %) in the composite were synthesized using zirconium oxychloride (ZrOCl₂·8H₂O) and graphene oxide as the starting materials. The photocatalytic activities of the synthesized composites were measured for the degradation of methyl orange dye with UV spectroscopy. The rate of decolorization was recorded with respect to the change in intensity of absorption peaks for methyl orange. The absorption peaks, diminished and finally disappeared during reaction, indicating that the dye had been degraded. The photocatalytic activity is strongly affected by the concentration of graphene in the ZrO₂. The synthesized ZrO₂/graphene photocatalysts are characterized by X-ray diffraction, TGA, Raman spectroscopy and

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UV–Visible spectroscopy. Finally, it has been concluded that graphene when employed as catalytic support for ZrO_2 boost its photo catalytic efficiency.

Keywords Photo catalytic \cdot Graphene oxide \cdot ZrO₂ \cdot XRD \cdot UV–Visible spectroscopy

1 Introduction

Photo catalysis, has been recently used for water decontamination [1]. Industries uses color for dyeing their products and unused color is released in water, the dyes used are non-biodegradable and harmful for flora and fauna. Traditional physical techniques used for water decontamination like adsorption on activated carbon, ultra filtration, reverse osmosis, coagulation by chemical agents etc. are only succeed in transferring organic compounds from water to another phase, thus creating secondary pollution [2]. On the other hand advance oxidation processes like Fenton [3] and photo Fenton catalytic reaction [4] are too expensive. In comparison to these techniques photocatalysis is economical and it completely oxidizes the organic pollutants to water and carbondioxide [2].

There are number of materials used for photocatalytic degradation such as TiO₂, ZnO, ZrO₂, WO₃, CdS, Bi₂WO₄, BiOCl, etc. [5]. Out of these, TiO₂ is the most popular material for photocatalysis because of its low cost and good semiconducting properties [5, 6]. To optimize the performance of TiO₂ as a photocatalyst several attempts have been made, like doping of suitable species [7–10]. For photo catalysis reaction important parameters are large surface area [7] that increases the absorption of UV light irradiated on the sample, secondly the prevention of recombination of electron hole pair produced during the

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reaction [5]. Both these requirements can be achieved by addition of graphene [7, 11] because of its large specific area $(2,630 \text{ m}^2/\text{g})$ [12] and highly conducting properties [13], facilitates the electrons to move ballistically in a graphene layer without scattering at ambient temperature, which makes graphene to perform as an excellent electron acceptor [7].

Liu et al. [14], Zhang et al. [15] observed that addition of graphene in TiO₂ have strong influence on its photocatalytic properties. Wang [7] and his coworkers found that degradation of acetone in air enhanced when graphene is added in TiO₂ and Degussa P25. Similar results have been reported by researchers when such studies were repeated with other photocatalytic materials such as ZnO, SnO₂, Cu₂O, Fe₂O₃, NiO, MnO₂ [5, 16, 17].

Despite so much work on photocatalytic activities of TiO_2 , there are some limitations while using it in photocatalytic reactors. It is because of its nonporous structure and low adsorption for pollutants [18]. Even addition of suitable species in TiO_2 did not enhance its photocatalytic activity significantly and were rather detrimental [18, 19].

Zirconium oxide (ZrO₂) is another suitable material for photocatalytic activities because of its semiconducting properties [5, 18], low thermal conductivity, water insolubility, catalysis [20–22] and optical properties [23, 24]. It is inorganic oxide, whose band gap estimates from 5–7 eV [25, 26] depending on the phase (cubic, tetragonal, monoclinic or amorphous) and preparation methods. Lopez et al. [18] found that photocatalytic activity of ZrO₂ can be enhanced when doped with suitable transition metal ions such Cu, Mn.

To the best of author's knowledge, no systematic study on the effect of graphene on the photocatalytic properties of ZrO_2 has been carried out so far. So in the present work, the experimental results obtained from study to explore the effect of graphene addition on photocatalytic properties of ZrO_2 are presented.

 ZrO_2 is synthesized by combustion method from zirconium oxychloride. Further, ZrO_2 /graphene (Zr–Gr) composites are synthesized by chemical reduction using hydrazine hydrate. The composite synthesized shows enhanced photocatalytic activity towards the degradation of the methyl orange dye UV light irradiation. The obtained results are compared with the similar studies carried out by other researchers on TiO₂ and other materials.

X-ray diffraction (XRD) was recorded by XPERT-PRO diffractometer (45 kV, 40 mA) equipped with a Gionometer PW3050/60 working with Cu K α radiation of wavelength 1.5406 Å in the 2 θ range from 5° to 80°.The photo catalytic analysis was carried out using a LAMB-DATM 650 UV/Vis/NIR spectrometer (Perkin Elmer, Inc., Shelton, CT USA).

2 Experimental

2.1 Materials

Graphite powder (purity 99.99 %), sodium nitrate (99.0 %), sulphuric acid, potassium permanganate (99 %), hydrogen peroxide, sodium borohydride, zirconium oxychloride, hydrochloric acid and hydrazine hydrate were used. All chemicals were used directly as received and stock solutions were prepared by using doubly deionized water. Methyl orange is an azo dye with the molecular formula $C_{14}H_{14}N_3NaO_3S$ (sodium-4-dimethyl amino-azo benzene-4 sulfonate) used as indicator in the photo catalytic experiment.

2.2 Synthesis of GO

GO is a water-soluble nanomaterial prepared through chemical attack on graphite powder to introduce oxygen containing impurities in graphite crystal. Modified Hummers' method was used to prepare GO by reacting the commercially obtained graphite powder, NaNO₃ and H_2SO_4 in the ratio of 1:1:23. KMnO₄ used as oxidizing agent was added slowly in above mixture [27], followed by stirring for 1 h at 40 °C. After that 100 ml water was added and solution was again stirred for 30 min at 90 °C. Subsequently, H_2O_2 was added to the reaction vessel to remove excess of KMnO₄. Solution was then filtered, washed with deionized water and dried in oven at 80 °C for 12 h. The GO has the appearance of brown color powder.

2.3 Preparation of ZrO₂

To prepare ZrO_2 powder, zirconium oxychloride was dissolved in distilled water and zirconium hydroxide was precipitated by drop wise addition of ammonium hydroxide (maintaining constant pH about 10.5) with stirring. The resulting mixture was filtered and washed with hot distilled water several times. Finally, the filtered paste was kept in oven at 100 °C for 12 h followed by calcination at different temperatures (400, 600 and 1,000 °C) for 2 h in furnace.

2.4 Preparation of Zr-Gr composites

The obtained ZrO_2 and GO were used as precursors to synthesize the Zr–Gr composite. ZrO_2 aqueous solution of concentration 0.1 M was prepared in distilled water, the GO and hydrazine hydrate (10 µl) was also added in it. Hydrazine hydrates act as a reducing agent to reduce GO into graphene. The mixture was refluxed for 36 h at 130 °C. After refluxing the solution was filtered and washed with deionized water and kept in oven at 80 °C for drying. The same procedure was repeated for different concentrations of GO with weight ratio of 5.7, 7.3, 8.3 % in ZrO_2 solution.

To study the photo catalytic properties of Zr–Gr using MO as an indicator, 4 mg MO have been taken in 500 ml deionized water and 0.2 μ l H₂O₂ was added to it. H₂O₂ provide oxygen during course of reaction. In 100 ml of prepared solution of MO, 150 mg of catalyst (ZrO₂ or Zr–Gr) was added and kept under UV irradiation and photo degradation was studied using UV–Visible spectroscopy.

3 Results and Discussion

3.1 TGA Analysis

Thermal stability of the natural graphite powder (NGP), GO, graphene and Zr-Gr composite was studied by using perkin elmer diamond TG/DTA analyser. Dried alumina powder was used as reference material for taking the thermograms. Samples were heated from ambient temperature to 700 °C in atmosphere of air at flow rate of 20 ml/ min. As shown in Fig. 1, thermogravimetry traces of NGP and Zr-Gr composite exhibited almost no weight loss during the whole heating process, whereas GO shows low thermal stability as compared to graphite due to reduced Vander Waal interaction because interlayer spacing is higher in GO. TGA results shows GO starts to lose mass upon heating even below 100 °C due to evaporation of water molecules that were held in the material. Significant weight loss of GO exhibits around 200-500 °C, presumably due to pyrolysis of the labile oxygen-containing functional groups to yield CO, CO₂, and steam [28]. Above 500 °C there is steady weight loss due to removal of more stable oxygen groups. As compared to GO graphene shows higher thermal stability and major weight loss occur near 400 °C.



Fig. 1 TGA of Graphite powder, GO, Gr and Zr-Gr composite

3.2 X-ray Diffraction

The XRD pattern in Fig. 2a shows the GO diffraction peak at $2\theta = 9.8^{\circ}$, and of reduced graphene at 22.8°. Which disappear in Zr–Gr composite (shown in Fig. 2b) indicating that the GO was reduced to graphene. Figure 2b shows the XRD spectrum of synthesized Zr–Gr (weight ratio 8.3 %) obtained after annealing ZrO₂ at different temperatures. Unannealed ZrO₂ shows amorphous pattern while sample Zr–Gr annealed at 400 °C shows prominent peaks at $2\theta = 30.08^{\circ}$, 35.13° , 50.06° , 59.9° , 62.67° corresponding to (101), (110), (200), (211), (202) tetragonal phase [29, 30]. The peaks corresponding to any other phase like monoclinic were not observed. Annealing of ZrO₂ at 600 °C and subsequently preparation of Zr–Gr composite show peaks at $2\theta = 24.4^{\circ}$, 28.40° , 31.6° , 34.5° , 40.96° ,



Fig. 2 a XRD of Graphite powder, GO and Gr. b XRD of Zr–Gr (8.3 %) annealed at 400, 600 and 1,000 $^\circ C$

Table 1 Phase of ZrO_2 and Zr-Gr (ZrO_2 annealed at different temperatures)

Temp (°C)	Phase						
	ZrO2	Zr-Gr (5.7 %)	Zr-Gr (7.3 %)	Zr–Gr (8.3 %)			
400	t	t	t	t			
600	45.5 %(m)	69.5 %(m)	73.3 %(m)	73 %(m)			
1,000	92.3 %(m)	m	m	m			

45.29°, 50.40°, 60.32°, 63.05°, which corresponds to monoclinic phase and few other peaks at $2\theta = 30.40^\circ$, 34.51° which corresponds to tetragonal phase of zirconia. Further Zr–Gr composite (ZrO₂ annealed 1,000 °C) adds new peaks at $2\theta = 49.08^\circ$, 56.99°, 57.94°, and 70.9° corresponding to monoclinic phase.

The amount of monoclinic, tetragonal and cubic phase content in pure zirconia powder are calculated by peak area of the monoclinic peak $(11\overline{1})$ and (111) versus tetragonal peak (111) using equation [29-32]

% M =
$$\frac{I(11\overline{1})m + I(111)m}{I(11\overline{1})m + I(111)m + I(111)t}$$

where I (111)m, I (111)m, I (111)t are area under the monoclinic peak (111), (111) and tetragonal peak (111) respectively. It has been calculated that ZrGr (annealed at 400 °C) is purely tetragonal in nature while at 600 °C it has 73 % monoclinic phase and 27 % tetragonal phase and at 1,000 °C it has monoclinic phase, So conclusion has been drawn that with increasing annealing temperature monoclinic phase increases and at intermediate temperatures (between 400 to 1,000 °C) it changes from cubic or tetragonal to monoclinic (Table 1).

The crystalline size of ZrO_2 powder has been calculated using Debye–Scherrer formula:

$$D = \frac{K\lambda}{\beta\cos\theta}$$

where D is the average crystallite size, K = correction factor (0.9), $\lambda = 0.154$ nm wavelength of Cu K α the peak width and θ the peak angle.

The values of crystalline size of pure zirconia (annealed at 400, 600, 1,000 °C) are 14.32, 26.5, 45.3 nm respectively. Whereas crystalline size of Zr–Gr (8.3 %) composite annealed at 400, 600 and 1,000°C has calculated 25.7, 27.2 and 33.9 nm respectively.

The dominance of monoclinic phase as compared to tetragonal (t) or cubic (c) increases with annealing temperature. The corresponding percentage of monoclinic phase in ZrO_2 and Zr-Gr (annealed at different temperatures) is summarized in Table 1.



Fig. 3 Raman spectroscopy for ZrO_2 and Zr--Gr~(8.3~%) annealed at 1,000 $^{\circ}C$

3.3 Raman Analysis

Figure 3 shows the Raman spectra of ZrO₂ and Zr-Gr (8.3 %) annealed at 1,000 °C. As predicted by factor group analysis, the monoclinic phase should have 18 $(9A_g + 9B_g)$ Raman active vibrational modes [33]. Raman frequency modes for monoclinic ZrO₂ ranging from 177 to 616 cm^{-1} [33, 34]. The spectrum of ZrO_2 (annealed at 1,000 °C) is formed by several well defined peaks that can be identified as the characteristic features of the Raman spectrum of ZrO₂ monoclinic phase. Raman active vibrational modes of monoclinic ZrO₂, are observed and they are assigned as follows: A_g at 177 cm⁻¹, B_g at 333 cm⁻¹, B_g at 381 cm⁻¹, A_g at 475 cm⁻¹, A_g at 558 cm⁻¹, A_g at 637 cm^{-1} . Besides, bands observed at 475 and 637 cm⁻¹ are observed in both tetragonal and monoclinic phases of ZrO₂ [30]. As graphene has incorporated into it than Zr-Gr (8.3 %) composite shows small shifting in monoclinic peaks of ZrO₂ due to interaction of ZrO₂ with Gr and some additional peaks at 1,345, 1,579, 2,695 cm⁻¹ corresponding to Gr.

3.4 Photo Catalytic Analysis

The photocatalytic activity of ZrO_2 and Zr–Gr was examined by analyzing the effect of annealing temperature and concentration of graphene on degradation of methyl orange dye in UV light.

3.4.1 Effect of Annealing Temperature and UV Irradiation Time

Figure 4a shows the absorbance of methyl orange with time under irradiation of UV light with using pure ZrO_2 (annealed at 400 °C) as photo catalyst. It was observed that the photo catalytic activity shows strong dependence on the UV irradiation time and degradation increases with increase in irradiation time.



Fig. 4 a–c Photo catalytic properties of ZrO₂ (Annealed at 400, 600 and 1,000 °C respectively). **e–g** Photo catalytic properties Zr–Gr (5.7 %) (ZrO₂ annealed at 400, 600 and 1,000 °C respectively). **h–j**

Photo catalytic properties Zr-Gr (7.3 %) (ZrO_2 annealed at 400, 600 and 1,000 °C respectively). **I-n** Photo catalytic properties Zr-Gr (8.3 %) (ZrO_2 annealed at 400, 600 and 1,000 °C respectively)

ZrO₂ surface gain more energy from UV light at higher exposure time, and due to this reason the degradation of methyl orange was increased with time. It was also observed that the photo degradation of MO was more for ZrO₂ annealed at higher temperatures. This effect may be observed due to decrease in band gap of ZrO2 with increase in annealing temperature [26], reduction in recombination centers and improved crystallinity at higher temperatures. This decrease in band gap was correlated with grains size increases with temperature, when the latter increases the defects and impurities tend to disappear causing a reorganization of the structure [33]. Improved crystallinity is important for OH group formation which acts as active sites for photo degradation [6]. In this study, the degradation of MO (Fig. 4a) for ZrO₂ annealed at 400 °C occur in 1 h 50 min, ZrO_2 annealed at 600 °C the degradation time (Fig. 4b) reduces into 1 h 30 min. Further, for ZrO₂

annealed at 1,000 °C the degradation time of MO (Fig. 4c) become 80 min.

3.4.2 Effect of Graphene

It was observed that when concentration of Gr is increased in ZrO_2 the degradation of MO occur faster than pure ZrO_2 .

The degradation of MO for ZrO_2 annealed at 400 °C with 5.7, 7.3, 8.3 % graphene in it occur in 1 h 40 min, 1 h 10 min and 1 h (Fig. 4d, g, j) respectively. For ZrO_2 annealed at 600 °C the degradation of MO after addition of same concentration of Gr results in change in degradation time to 80, 60 and 51 min (Fig. 4e, h, k). Further for ZrO_2 annealed at 1,000 °C with graphene (5.7, 7.3, 8.3 %) in it, the MO degradation time reduced to 67, 55 and 45 min (Fig. 4f, i, 1). The degradation time of various samples are shown in Table 2.

Material	Degradation time	Material	Degradation time	Material	Degradation time	Material	Degradation time
ZrO ₂ (400 °C)	110	ZrO ₂ (400 °C)/ Gr (5.7 %)	100	ZrO ₂ (400 °C)/ Gr (7.3 %)	70	ZrO ₂ (400 °C)/ Gr (8.3 %)	60
ZrO ₂ (600 °C)	90	ZrO ₂ (600 °C)/ Gr (5.7 %)	80	ZrO ₂ (600 °C)/ Gr (7.3 %)	60	ZrO ₂ (600 °C)/ Gr (8.3 %)	51
ZrO ₂ (1,000 °C)	80	ZrO ₂ (1,000 °C)/ Gr (5.7 %)	67	ZrO ₂ (1,000 °C)/ Gr (7.3 %)	55	ZrO ₂ (1,000 °C)/ Gr (8.3 %)	45

Table 2 The degradation time of MO for ZrO₂ (annealed at different temperature) and for Zr-Gr composite



Fig. 5 Degradation versus time variation of, **a** ZrO_2 (annealed at 400 °C) and Zr–Gr having different conc. of Gr (5.7, 7.3, 8.3 %). **b** ZrO_2 (annealed at 600 °C) and Zr–Gr having different conc. of Gr

(5.7, 7.3, 8.3 %). c ZrO₂ (annealed at 1,000 °C) and Zr–Gr having different conc. of Gr (5.7, 7.3, 8.3 %)

Degradation factor (X) at any time can be calculated by equation

$$X = \frac{C_o - C}{C_o}$$

where C_o is the initial concentration and C is the concentration of MO at any time.

Figure 5 shows the variation of degradation factor with time and it has been concluded that Zr–Gr composite which have higher concentration of graphene degrade the MO more rapidly for same annealing temperature of ZrO_2 . With addition of graphene in ZrO_2 , the degradation time decreases and degradation factor is enhanced. For Zr–Gr composite degradation is faster in composite which have higher concentration of Gr.

This effect of graphene addition on degradation constant may be due to the shifting of e^- to graphene immediately after generation of $e^- h^+$ pair when UV light falls on Zr–Gr composite. Graphene with excess of electron react with oxygen and create superoxide oxygen anion (O₂^{-*}) and ZrO₂ having excess hole (ZrO₂ (h +)) react with hydroxyl anion and change it to hydroxyl radical (OH*). Both superoxide oxygen anion and hydroxyl anion react with dye and degrade it. The photogenerated electrons drive the water-splitting reaction to produce hydrogen [8, 35, 36]. The degradation reactions take place in the interphase region between the liquid and photoexcited solid [37].

The reaction occurs at the time of photocatalysis on the surface of Zr–Gr are shown below:

$$\begin{split} & ZrO_2 + hv \ \rightarrow e^- + h^+(at \ the \ ZrO_2 surface) \\ & ZrO2(e^-) + \ Graphene \rightarrow ZrO2 + \ Graphene \ (e^-) \\ & Graphene \ (e^-) + \ O2 \rightarrow Graphene \ + \ O_2^{-*} \\ & ZrO_2(h+) + \ OH^- \rightarrow ZrO_2 + \ OH^* \\ & OH^* + \ MO \ dye \rightarrow Degradation \ products \end{split}$$

The importance of hydroxyl ions on photocatalytic reaction is clearly indicated in above set of chemical reaction steps. Photoluminescence (PL) study by Xiang et al. also experimentally confirmed that hydroxyl radicals are most active species for photo catalysis [6].

So it can be concluded that degradation of MO enhanced at higher annealing temperature of ZrO_2 and at higher graphene concentration. This is mainly due to the fact that high quality of the sp² conjugated bond in the carbon lattice of graphene enhances the light absorption range, promote charge separation [38] and increase adsorption of pollutants. Similar studies by Liu et al. [14] on TiO₂/Gr indicate 80 % photocatalytic degradation of MO. Cao et al. [39] and Zhang et al. [15] also reported enhancement in degradation constant of MO up to 100 % (within 120 min) and 85 %, respectively when graphene was added in TiO₂. Madhusudan et al. [17] observed

similar results for $Bi_2O_2CO_3$ when graphene was added into it.

So, the experimental results obtained from present study are in close agreement with the results reported earlier in the literature. However, in this report, using ZrO_2 with 8.3 % graphene, 98 % degradation was observed in a lesser time i.e. 45 min which shows higher improvement in photocatalytic degradation as compared to those observed earlier in other metal oxides.

4 Conclusions

Zr-Gr composites have been successfully synthesized using solution based method. Raman spectra clearly indicates the reduction of GO into Gr and the strong interaction between ZrO₂ and Gr. The prepared Zr-Gr composite shows the enhanced photocatalytic activity towards degradation of MO. It has been concluded that degradation of Methyl orange dye increases with increase in the concentration of graphene in ZrO₂. This fact is due to the electron separation and transportation properties of graphene due to which electron hole pair obtained during photo catalysis reaction is shifted to graphene and electron hole recombination cannot occur. So, both electron and hole can take part in photo catalytic reaction more effectively. Also reaction rate increase with increase in the annealing temperature of ZrO₂. Hence prepared composite is useful in environmental and energy-related applications.

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