

Preparation and photocatalytic activity of anatase titania modified with dysprosium oxide

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ABSTRACT

The growth of industry worldwide has tremendously increased the generation and accumulation of waste byproducts. This has caused severe environmental problems that have become a major concern. One of the important techniques for removing industrial waste is the use of light energy and particles sensitive to this energy to mineralize waste, which aids in its removal from solution. TiO_2 is considered as an ideal semiconductor for photocatalysis because of its high stability, low cost and safety toward both humans and environment. TiO_2 has a wide band gap which prevents the utilization of visible light that constitutes a major portion of solar energy. Fabrication of new or modified semiconductor photocatalysts such as doped systems, dye sensitized systems or small band gap semiconductors that are active under Visible light is still a challenge. The present study aims to examine the photo catalytic activity of TiO_2 and its modified system using Dysprosiumoxide. Modification is done by wet impregnation method. The Photocatalytic activity of the prepared systems was studied by analyzing in Coomassie Brilliant Blue R-250 removal from synthetic wastewater.

KEY WORDS: modified Titania, Photocatalytic activity, dye degradation.

1. INTRODUCTION

Titania has emerged as one of the most fascinating materials in the modern era due to its inertness to chemical environment and long-term photo stability, which in turn renders its applications in various fields like science, technology and environment. These applications depend not only upon the properties of TiO_2 itself, but also on the crystalline modifications of TiO_2 . TiO_2 is tuned to combat various environmental pollution especially in the removal of unwanted impurities from water, air, etc. owing to its photocatalytic property. Highly efficient use of TiO_2 nanomaterials is occasionally prevented by its wide band gap ($E_g = 3.2$ eV for the anatase form) which allows radiation absorption only near-UV range of approximately 388 nm or less, which accounts only 3–4% of solar radiation. One of the goals for improving of the performance of TiO_2 nanomaterials is modifying it as a visible responsive catalyst (Shi, 2014). In recent years, extensive research works have focused on visible-light induced photocatalysis by metal ion-doped semiconductor, to achieve extended absorption spectra into visible-light region. This property has been explained by the excitation of the electrons of dopant ion to the conduction band of semiconductor (i.e., a metal to conduction band charge-transfer). Numerous metal ions including transition metal ions (e.g., vanadium, chromium, iron, nickel, cobalt, ruthenium and platinum) and rare earth metal ions (e.g., lanthanum, cerium, and ytterbium) have been investigated as potential dopants for visible-light induced photocatalysis (Saif, 2007; Liu, 2008; Choi, 2007; and Dou, 2001).

The present work is aimed at examining the photocatalytic activity of TiO_2 and its Dysprosium oxide modified system of towards the decomposition of Coomassie brilliant blue dye. Modification of titania is achieved by wet impregnation method. The systems are characterized by X-Ray diffraction analysis (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Fourier Transform Infra-Red (FT-IR) spectroscopy, UV-VIS Diffuse Reflectance spectroscopy (UV-VIS DRS), and surface area analysis by BET method. The photocatalytic activity of all the systems was examined by photodegradation of Coomassie Brilliant Blue dye under UV and Visible light irradiation.

2. EXPERIMENTAL

2.1. Materials: Titanium (IV) oxide, Anatase (Sigma-Aldrich) was used as the pure titania phase. Dysprosium (III) nitrate hexahydrate, $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich), was used as the dopant metal precursor. Deionized water was used throughout the experiment.

2.2. Preparation of doped TiO_2 system: Wet- Impregnation method is used for the preparation of doped TiO_2 catalyst. 8 % metal oxide doping is done on TiO_2 for preparing the modified systems. For preparing Dy doped TiO_2 system, about 24g of TiO_2 powder was added to 72 ml aqueous solution of Dysprosium nitrate hexahydrate under constant stirring for 3 hours at room temperature. The solvent was evaporated slowly in a water bath at 80^o C. The sample was oven dried at 110^o C and calcined at 400^o C for 4 hours. Prepared catalyst is represented as $\text{TiO}_2\text{-Dy}_2\text{O}_3$ system.

2.3. Characterisation of the prepared Catalysts: Morphology of the prepared samples was analysed by Scanning Electron Microscopy experiments using Stereo scan 440 Cambridge, UK. X-ray Powder Diffraction (XRD) studies using Rigaku D/MAX- diffractometer with CuK_α radiation determined the crystalline phase of the samples. Jasco V- 550 spectrometer was used to record UV – VIS DRS spectra of the samples using BaSO_4 as reference. Jasco 4100 model instrument was used for recording FTIR spectra of the powder samples by the KBr disk method over the range $400 - 4000 \text{ cm}^{-1}$ and the BET surface areas of the catalyst samples were measured by N_2 adsorption at -197°C using Micromeritics Gemini surface area analyzer.

2.4. Photocatalytic Activity studies: In order to examine the photocatalytic activity of Titania doped system, the photodegradation of Coomassie Brilliant Blue dye has been investigated in aqueous heterogeneous suspensions equipped with UV (SAIC, 150W) and Visible (SAIC, 400W) radiation sources. A biannular quartz glass reactor with the lamp immersed in the inner part was used for all Photocatalytic experiments. The reactor is provided with a water circulator and a stirrer. Degradation study was performed using 10^{-5} M aqueous solution of CBB dye in which the catalyst amounts to 1 g/l . Before illumination all the experiments were performed in dark with constant stirring in order to find out whether there is any decrease in the concentration due to adsorption. Aliquots of the aqueous suspension were collected at regular time periods during irradiation and the catalysts and solution were separated by centrifugation; the collected samples were analyzed by UV-Vis spectrophotometer (Shimadzu UV-1700). The concentration of the solution collected at regular intervals of time was calculated for each sample using Beer Lambert law

$$A = \epsilon Cl.$$

Where A is the absorbance, L is the path length in cm, ϵ is the molar extinction coefficient having unit $\text{Lmol}^{-1}\text{cm}^{-1}$, and c is the concentration in molL^{-1}

The photodegradation efficiency of CBB has been calculated by applying the following equation:

$$\% \text{ photodegradation efficiency} = (C_0 - C)/C_0 \times 100$$

Where C_0 is the original CBB content, C is the retained CBB in solution.

3. RESULTS AND DISCUSSION

3.1. Scanning Electron Microscopy (SEM): Typical scanning electron micrograph of the catalysts samples is shown in Fig.1. The morphology of the particles was found to be polygonal. The morphology of the Dysprosium doped sample did not show any commendable morphological change when compared with the undoped system. Average particle size distribution of both doped and undoped sample was observed to be in the range of 50 to 200 nm.

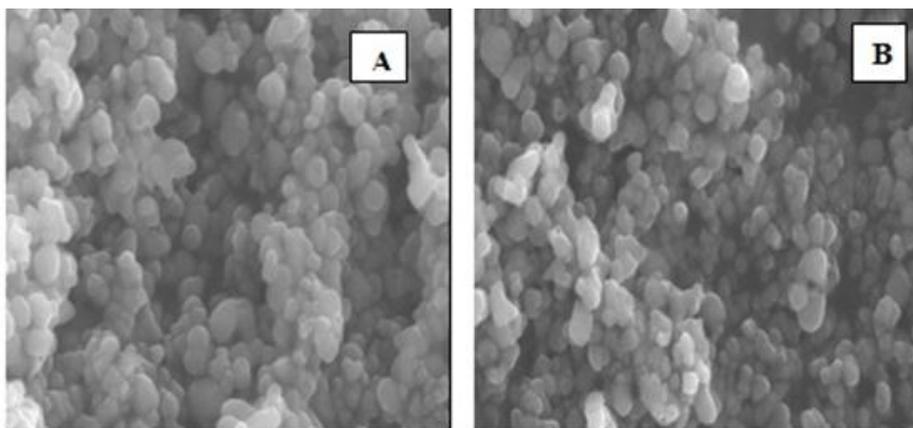


Figure.1. SEM images of [A] Commercial titania and [B] $\text{TiO}_2\text{-Dy}_2\text{O}_3$

3.2 Transmission Electron Microscopy (TEM): The scanning electron micrograph of commercial Titania (Fig.1) hints to aggregated particles in the range 50 -200 nm. The same observation is also made from the TEM image displayed in Fig.2, which exhibited aggregated polygonal particles of above mentioned size in both doped and undoped samples.

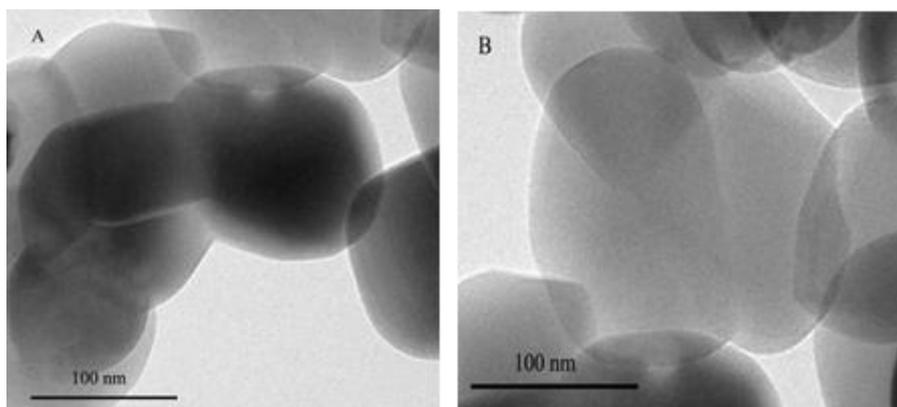


Figure 2. TEM images of [A] Commercial titania and [B] $\text{TiO}_2\text{-Dy}_2\text{O}_3$

3.3. X-Ray Diffraction Studies (XRD): The x-ray diffraction pattern of commercial Titania and Dysprosium doped samples are shown in Fig. 3. The sharp well defined peaks show high crystallinity of the sample. Major peaks are observed at 2θ values 25.42, 37.05, 37.87, 38.66, 48.05, 54.02, 55.18, 62.77, and 68.83 degree corresponding to d values 3.50, 2.42, 2.37, 2.32, 1.89, 1.69, 1.66, 1.47, and 1.36 nm which are characteristic of anatase phase. The particle size was calculated by the Scherrer formula and was found to be 21.9 nm in the case of commercial system. For the dysprosium doped titania system, the peaks are similar to that of pure Titania indicating the Dy_2O_3 formed is uniformly dispersed on the surface of Titania. The particle size of Dy doped TiO_2 was estimated by the Scherrer formula and was obtained as 47.07 nm.

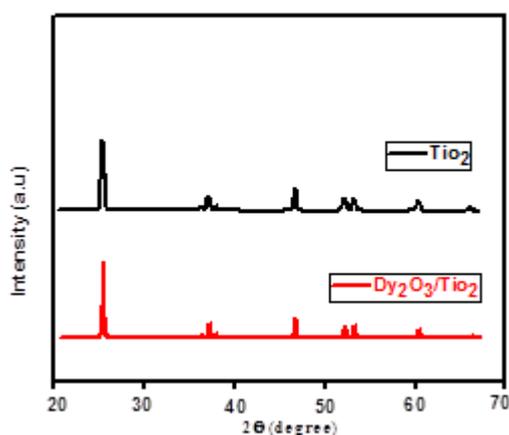


Figure.3. XRD pattern of undoped and doped samples

3.4. UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS): When compared to the UVDRS spectrum of pure TiO_2 , the absorption edge of $\text{Dy}_2\text{O}_3/\text{TiO}_2$ system was shifted to longer wavelength region. Thus it can be inferred that the dopant is effective for visible light response. The Kubolka- Munk (K-M) function, $F(R_\infty)$ is extracted from the UV-Vis DRS absorbance and the band gap energy (E_g) for allowed transitions is determined by finding the intercept of the straight line in the low energy rise of the plot of $[F(R_\infty)h\nu]^2$ against $h\nu$, where $h\nu$ is the incident photon energy (Yu et al., 2006). The band gap of pure TiO_2 and $\text{TiO}_2\text{-Dy}_2\text{O}_3$ was calculated from Kubolka-Munk plot and are found to be 3.21 eV and 3.08 eV respectively. It is clear that the band gap of $\text{TiO}_2\text{-Dy}_2\text{O}_3$ is indeed lower than Titania (3.21 eV).

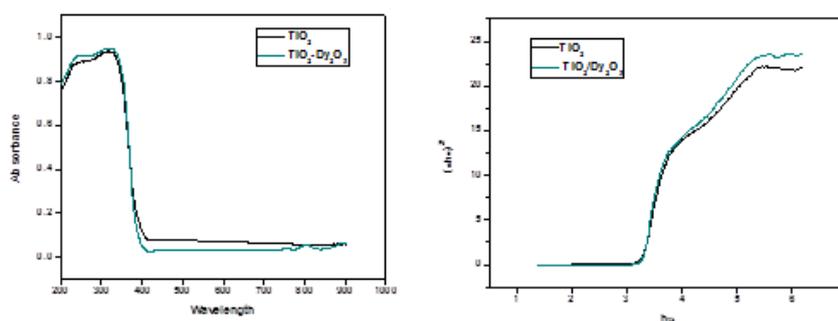


Fig. 4. UVDRS absorption spectrum and the corresponding Kubolka – Munk plot of TiO₂ and TiO₂ - Dy₂O₃ systems

3.5. Fourier transform Infra –Red spectroscopy (FTIR): The FTIR spectrum of the anatase titanium oxide and TiO₂/Dy₂O₃ samples are shown in Fig.5. The FTIR spectrum shows a broadband at 3424.92 cm⁻¹ which is attributed to the O-H stretching mode of the surface adsorbed water molecule. Another band at 1634 cm⁻¹ is attributed to the O-H bending mode of physically adsorbed water. The bands at 537.56 and 684.73 cm⁻¹ are due to the Ti-O bond stretching mode of Titania. In the case of TiO₂/Dy₂O₃ samples the peaks are similar to that of pure Titania and there are no characteristic peaks of dysprosium indicating the Dy₂O₃ formed is uniformly dispersed on the surface of Titania. A broadband located at 1638.92, 3422.52 cm⁻¹ is ascribed to the O-H bending and stretching vibration of residual water and hydroxyl groups. The absorption band at 1384 cm⁻¹ which is attributed to the presence of nitrate group could not be detected on the spectrum indicating that the calcination process was able to completely remove the nitrate group from the raw catalyst.

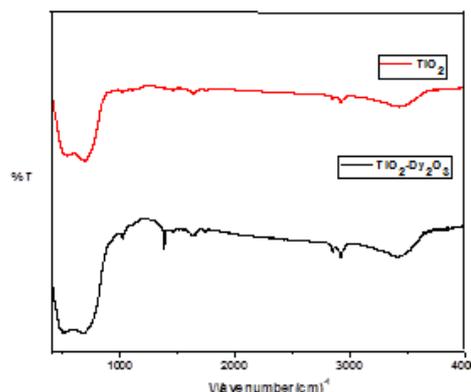


Figure.5. FTIR spectra of (A) TiO₂ and (B) TiO₂-Dy₂O₃

3.6. Surface area: The surface area of pure commercial TiO₂ and its modified metal oxide system determined by N₂ adsorption method using BET approach are given in Table 1. The surface area of pure Titania is 56 m²/g. It can be seen that there is a significant reduction in surface area of Dysprosium doped system when compared to pure Titania and it was 10.06 m²/g.

Table.1. Surface area of doped and undoped sample

Sample	TiO ₂	TiO ₂ -Dy ₂ O ₃
Surface Area	56 m ² /g	10.06 m ² /g

3.6. Photocatalytic Activity Studies:

3.6.1. Degradation of CBB over Titania doped system: The photo catalytic activity of the catalysts was studied by measuring the degradation of aqueous solution of Coommaassie Brilliant Blue dye in UV and Visible light. Degradation of this dye can be monitored from the disappearance of blue colour by UV-Visible spectroscopy. Since considerable degradation was observed at 30 minutes for almost all systems, that time have been selected as the time of reaction for comparing the catalyst activities. The concentration of CBB dye is proportional to its absorbance according to the Beer–Lamberts law. For comparison, the photo degradation study was performed for the undoped system. The data obtained from UV Visible spectrometer for the prepared systems was plotted as a function of absorbance versus wavelength.

3.6.2. Dye degradation under UV radiation and Visible radiation: Table 2 shows the percentage of degradation of CBB dye calculated after thirty minutes of reaction. The percentage of degradation increases after doping a dysprosium oxide on Titania. A uniform dispersion of the dopant on TiO_2 facilitates migration of electrons from its conduction band to that of Dy_2O_3 and this trigger the increased photocatalytic activity of $TiO_2-Dy_2O_3$. This is explained by Bandara (2005), in earlier studies (Fujishima, 2007; Mor, 2006; Linsbiegler, 1995; Yasomane, 2008; and Bandara, 2005). Presence of Dy_2O_3 in highly dispersed state has already been confirmed from the XRD pattern of the sample. Pure Titania was less active under visible light and the doped analogue exhibited commendably higher photo degradation activity of CBB dye. The trend in activity among the catalysts is justifiable using the same explanation provided in the case of reactions under UV radiation.

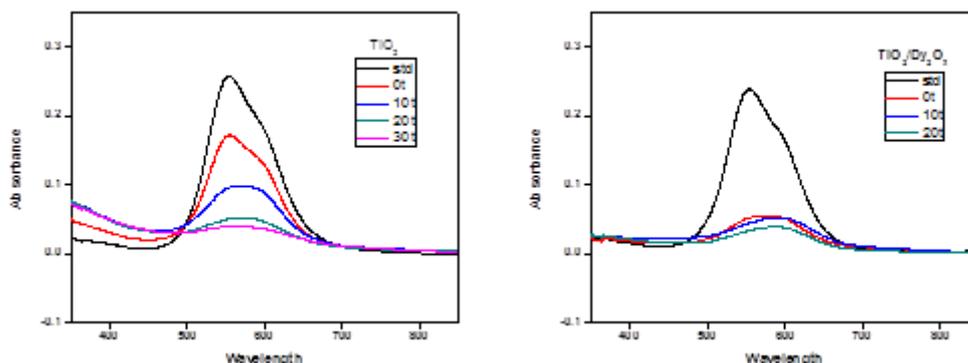


Figure.6. UV- Visible absorption spectral changes of CBB aqueous solution degraded in the presence of undoped and doped catalysts using UV lamp

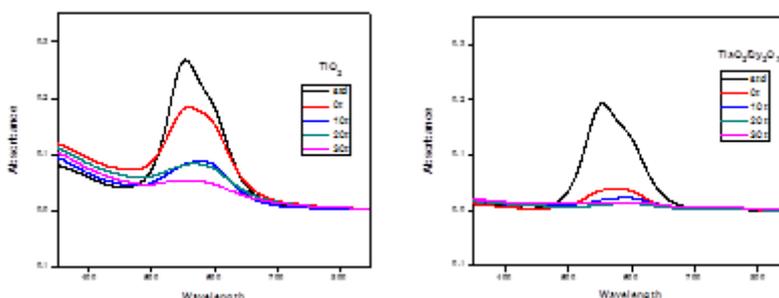


Figure.7. Visible absorption spectral changes of CBB aqueous solution degraded in the presence of undoped and doped catalysts using visible lamp

Table 2. Percentage of degradation of CBB dye after 30 minutes (UV light and Visible light)

Catalyst	% of degradation (UV Light)	% of degradation (Visible Light)
TiO_2	68.34	33
$TiO_2-Dy_2O_3$	85.3	94.8

4. CONCLUSION

Our study concentrated on the photocatalytic activity study of Titania and its Dysprosia modified system under UV and Visible radiations towards the decomposition of CBB Dye. Modification was done using metal oxide dysprosia. 8% of Dy_2O_3 was loaded on Titania by wet impregnation method. This metal oxide is proved to be good degradation capability. Prepared doped Titania system showed higher photocatalytic activity than commercial TiO_2 for decomposition of CBB dye in UV and Visible light. The shifting of the absorption band to the visible region observed in UVDRS spectrum is also in agreement with the above data. The improvement in photocatalytic activity depends on the efficiency of charge capture by the doping center. Doping can effectively slow down the recombination rate of the photogenerated electron-hole pairs and

enhances the interfacial charge-transfer efficiency and also uniform dispersion of the dopant on TiO₂ facilitates migration of electrons from its conduction band to that of Dy₂O₃ and this triggers the increased photocatalytic activity of TiO₂-Dy₂O₃.

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