Visible Light Driven Photocatalytic Activity of TiO$_2$ Nanoparticles Prepared via Gel-Combustion Process

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Abstract. A facile and cost-effective preparation of nanoscale TiO$_2$ with enhanced surface area was achieved through gel-combustion technique assisted via glycine as a fuel. X-ray diffraction studies confirmed the anatase phase and nanocrystalline formation of TiO$_2$ nanoparticles (NPs). Using N$_2$ adsorption-desorption curve, the enhanced surface area ($54.3$ m$^2$g$^{-1}$) of TiO$_2$ NPs was noted. Visible light driven photocatalytic activity of the TiO$_2$ NPs for the degradation of Methylene Blue (MB) dye was studied. The complete degradation of MB dye under sunlight irradiation was achieved in 120min. All the outcomes show that prepared TiO$_2$ nanoparticles have excellent visible light driven photocatalytic activity for the active degradation of MB dye.

1. Introduction
Titanium dioxide (TiO$_2$) has receiving significant consideration because of its intriguing properties that permit its applicability in a wide scope of utilizations, for example, pigments, medicine and gas detecting devices [1-4]. Specifically, the consideration has been as of late centered around the semiconducting and photosensitive conduct, abused in a few applications concerning the environmental field, for example, cleaning of air and water from contaminants and photovoltaic gadgets [5, 6]. TiO$_2$ as one of best semiconducting photo-catalytic material has gaining foremost enthusiasm for the moderation of ecological pollutants attributable to its compound and photo resistive character, simple and monetary accessibility, high absorption and appropriate electronic structure. Besides its wide band gap of 3.2 eV turns into a thorn for its movement under visible light. The morphology of the TiO$_2$ nanoparticles altogether influences their synergist and electrical conduct, with the goal that an incredible exertion has been made in the advancement of imaginative procedures for getting nanosized particles. A few new procedures and advancements have been created lately for the creation of titanium dioxide nanopowders, for example, gas-condensation [7], spray pyrolysis [8, 9], sol gel [10, 11], coprecipitation [12] and hydro-thermal [13]. The gel-combustion process, is an incredible technique for the fabrication of metal oxide nanoparticles [14-16]. The procedure, created toward the start of the nineties, is acted in the center between sol gel and combustion, consolidating compound gelation methods and combustion procedures. It depends on the Pechini preparation and it
utilizes a redox mixtures, containing an oxidizer and a fuel compound. The procedure includes an exothermic decomposition response of a fluid gel and a thermally initiated anionic redox response [17]. The response produces nanostructured powders at rather low temperatures. The powders are marginally reinforced into delicate and exceptionally permeable agglomerates. The gel-combustion process has been broadly utilized in the most recent years for the fabrication of nanoparticles of various metal oxides [18, 19]. The present work reports the gel combustion synthesis of TiO$_2$ nanoparticles (NPs) and its visible light driven photocatalytic activity for active degradation of Methylene Blue (MB) dye.

2. Experimental

Nano scale TiO$_2$ sample was prepared by gel combustion synthesis assisted via Glycine as a chelating agent. All the chemical were purchased from Merck (99.9% Pure) and used without further purification. In brief, titanium chloride solution was diluted in DH$_2$O and ammonium hydroxide solution was then added drop-by-drop into solution to adjust the pH of the solution as 7 which subsequently results into precipitate. The precipitate was collected by centrifuge machine and washed several times by DH$_2$O. Further the titanyl nitrate solution was prepared by adding precipitate into nitric acid. Glycine was further added into titanyl nitrate solution and complete solution was stirred and heated at 90$^\circ$C for 3h. Further, the solution was converted into gel and then combustion process take place. The combustion process results into formation of loose powder which then grinded using pestle mortar. The fine powder was then sintered at 500$^\circ$C for 4h for better crystallinity and used for further studies. The flowchart of the gel-combustion synthesis of TiO$_2$ nanoparticles is shown in Fig. 1. The phase formation and nano scale preparation of prepared sample was studied through X-ray diffractometer (Bruker-D8 Advance) in the 2$\theta$ range of 10$^\circ$ to 80$^\circ$ at ambient temperature. The surface area measurement was carried out by recording N$_2$ adsorption-desorption curve using Quantachrome instrument. The detailed procedure for surface area measurement is given in our previous reports [20, 21]. The time dependant dye degradation plots of TiO$_2$ nanoparticles was recorded by measuring UV-Vis absorbance spectra.

![Flowchart for gel-combustion synthesis of TiO$_2$ NPs](image-url)
3. Results and discussion

3.1. Structural analysis
The nano-scale formation and phase analysis of prepared sample was analyzed by XRD studies. Fig. 2 shows the XRD pattern of prepared TiO$_2$ NPs prepared by glycine assisted gel-combustion synthesis. The careful observation of Fig. 1 reveals that pure tetragonal anatase phase was appeared which well matches with the JCPDS card No. #01-084-1286 [22]. The average crystallite size was calculated using Debye-Scherrer’s formula [23-25] which found to be as 15 nm.

![X-ray diffraction pattern of TiO$_2$ NPs](image)

**Fig. 2** X-ray diffraction pattern of TiO$_2$ NPs

3.2. Surface area analysis
Surface area is one of the important parameters of nano-scale photocatalyst which significantly affects the photocatalytic activity of the materials. In the present case, the surface area measurements were done by well known BET method. The N$_2$ adsorption-desorption curve of the prepared TiO$_2$ NPs is shown in Fig. 3. The BET surface area calculated form N$_2$ isotherm was noted as 54.3 m$^2$g$^{-1}$ which is quite good as compared to other reports [26-28].

![N$_2$ adsorption-desorption curve for TiO$_2$ NPs](image)

**Fig. 3** N$_2$ adsorption-desorption curve for TiO$_2$ NPs
3.3. Photocatalytic activity
Visible light driven photocatalytic activity of the TiO$_2$ NPs for Methylene Blue (MB) dye degradation was studied by UV-Vis absorbance spectroscopy [29-31]. The time dependent MB dye degradation efficiency of the TiO$_2$ NPs under sun light irradiation is shown in Fig. 4. It is observed from Fig. 4 that, the maximum absorbance around 550nm was observed for pristine MB dye solution. With respect to time the absorbance get decreased which shows the effective degradation of MB dye solution. After 120 min, the complete degradation of MB dye was observed. These results shows that prepared TiO$_2$ NPs have excellent visible light driven photocatalytic activity for the active degradation of MB dye. The schematic of visible light driven MB dye degradation using TiO$_2$ NPs is shown in Fig. 5.

![Fig. 4 Time depended MB dye degradation plot for TiO$_2$ NPs](image)

![Fig. 5 Schematic of visible light driven MB dye degradation using TiO$_2$ NPs](image)

4. Conclusions
A facile and cost-effective preparation of nanoscale TiO$_2$ with enhanced surface area was achieved through gel-combustion technique assisted via glycine as a fuel. X-ray diffraction studies confirmed the anatase phase and nanocrystalline formation of TiO$_2$ nanoparticles (NPs). Using N$_2$ adsorption-desorption curve, the enhanced surface area (54.3m$^2$g$^{-1}$) of TiO$_2$ NPs was noted. Visible light driven
The photocatalytic activity of the TiO$_2$ NPs for the degradation of Methylene Blue (MB) dye was studied. All the outcomes show that prepared TiO$_2$ nanoparticles have excellent visible light driven photocatalytic activity for the active degradation of MB dye.

**Acknowledgement**

The author Sandeep B. Somvanshi acknowledges Department of Science and Technology (DST), Government of India for DST-INSPIRE Fellowship (IF170288).

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