Research

Investigation of photocatalytic activity of TiO$_2$ nanoparticles synthesized by sol–gel technique

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Abstract
Anatase phase TiO$_2$ nanoparticles were synthesized by sol–gel method using titanium(IV) butoxide as a starting material. The pH of solution was maintained by adding HNO$_3$ and NaOH. The obtained powder was heat-treated at 350 °C for 2 h. The XRD study shows that the crystalline size and crystallinity of samples increase with pH of solution. Raman spectra confirm the dominance of anatase phase of TiO$_2$. Morphology study of samples was done by scanning electron microscope (SEM). The size of prepared samples was calculated by XRD and confirmed by TEM analysis. The energy bandgap was calculated by optical absorption spectra and it was found to decrease by increasing pH of the solution. The photodegradation activity of Indigo Carmine (IC) dye under visible light irradiation was carried out by synthesized TiO$_2$ nanoparticles. The removal of Indigo Carmine dye and degree of mineralization after photodegradation were studied using HPLC and TOC analysis respectively.

Keywords TiO$_2$ nanoparticles · Absorption study · PL study · Indigo Carmine dye · Photodegradation

Introduction
In present days, the wastewater from industries found colorful liquid/dye which contains aromatic rings and metallic and halide ions, which are toxic to human health as well as aquatic life [1]. Such toxic water from industries is directly sent to the nearby rivers, ponds, and lakes which reduces the quality of water [2]. There are various methods in order to remove colorants from wastewater such as adsorption, flocculation, ozonation, and photocatalysis. Among all techniques, photocatalysis is low cost, ecofriendly, efficient, and reusable to decompose colorants [3, 4]. There are several metal oxide nanoparticles used as a photocatalyst because of their different physical and chemical properties better than bulk materials [5]. In a semiconductor nanomaterial, due to small size, motion of charge carriers is controlled by quantum confinement [6]. Large surface area of nanoparticles is useful in making interaction between material and medium. Especially, TiO$_2$ had been studied widely as a photocatalyst due to its great photochemical activity, non-toxicity, low-cost production, and high dielectric constant. Also, the oxygen atoms on the surface of TiO$_2$ take part in oxidation–reduction reaction [7, 8]. Some studies reveal that the co-doped TiO$_2$ with metals was used to eliminate the biological pollutants present in indoor air [9].

TiO$_2$ is synthesized by several methods like sol–gel, hydrothermal, CVD, microwave, and ball milling [10–13]. Among all these methods, the sol–gel process is the most interesting and easy method. It requires low temperature, easy process, high degree of purity, and homogeneity. It is also advantageous to regulate grain size, crystalline size, and morphology. However, TiO$_2$ has three crystalline phases namely anatase, brookite, and rutile. Among these three phases, rutile is stable while brookite and anatase are metastable phases [14]. The high photoreactivity of TiO$_2$ is obtained in the anatase phase which is metastable. Studies were carried out to find a new form of TiO$_2$ which is known as black TiO$_2$. The black TiO$_2$ forms defect states inside the material and increase the light interaction with material and show improvement in photocatalysis activity [15]. TiO$_2$ prepared by sol–gel technique was prepared and used for the photocatalytic application by many researchers [16–20]. The efficiency was reported for IC dye degradation varying from 50 to 100% in UV light [21–24]. So far, maximum efficiency...
for IC dye degradation using TiO₂ is found to be 100% in UV light for 2 h but not yet reported in visible light [23].

In the present study, an attempt is made to use TiO₂ in visible light for IC dye degradation. In this paper, anatase TiO₂ is synthesized by the sol–gel method, and the effect of pH on crystalline size, morphology, and optical properties is studied. Also, TiO₂ is used for the degradation of IC dye in visible light.

**Experimental**

TiO₂ nanopowder was prepared by simple sol–gel method. Titanium (IV) butoxide (supplied by Sigma-Aldrich 97%) was used as Ti precursor, titanium(IV) butoxide (40 mmol) was mixed with ethanol (50 ml). After mixing, it was stirred magnetically for 45 min at room temperature. In another beaker, a solution of deionized water (having different pH = 1, 3, 5) and ethanol was taken to use as a catalyst to promote hydrolysis. The pH of the solution was maintained by adding HNO₃ (supplied by Sigma-Aldrich 65%) or NaOH. Mixture of deionized water and ethanol was added drop-wise in a precursor solution; during this process, the precursor solution was heated up to 50 °C and the temperature was maintained during the reaction. This solution was stirred for 3 h which gives a clear white solution. The obtained sol was kept for gel formation for 24 h at room temperature which gives high viscous suspension. This viscous suspension was then washed with ethanol and deionized water for several times and dried at 90 °C for 15 h in a vacuum which gives a white powder. The various powder samples of TiO₂ were prepared by maintaining the different pH of the solution (pH = 1, 3, 5). The prepared samples were heat-treated at 350 °C for 2 h and named as p1_350, p3_350, and p5_350 [25].

**Characterization of TiO₂**

Crystalline nature of powder sample was studied by XRD (Bruker AXS D8 Quest System) using Cu as a target (CuKα1 = 1.5406 Å) at 40 mA and 45 kV. XRD measurement was carried out in the range from 15° to 80° with a step size of 0.017. The Raman spectra of samples were recorded using a Raman spectrometer (NOST: HEDA-URSM4/5/7). Morphological study of samples was done using a scanning electron microscope (SEM – ZEISS EVO18). The TEM analysis was carried out using TEM – Thermofisher:Talos F200 S. Absorption spectra of Indigo Carmine dye and UV–vis DRS of all prepared samples were recorded using UV–vis NIR spectrophotometer (JASCO, V-670). UV–vis diffuse reflectance spectra (UV–vis DRS) of samples were recorded at room temperature in the wavelength range of 300 to 500 nm using a spectrophotometer equipped with an integrating sphere accessory. Barium sulfate was used as a reference for the reflectance spectra. Photoluminescence spectra (PL) were recorded using JASCO FP-8200 spectrophotometer. The degraded products of Indigo Carmine dye were detected by the HPLC system (HPLC-Shimadzu UFLC series, 8040 model) equipped with a photodiode array detector. The mobile phase of phosphate (2.5 × 10⁻⁴ mol/L) to methanol ratio 30:70 was passed through separation column C18. All the measurements were carried out at room temperature at flow rate 1 ml/min. Total organic carbon (TOC) analysis was done using TOC-analyzer (Make- Shimadzu Japan, TOC-VCPH).

**Photocatalytic degradation of IC dye**

The catalytic performance of prepared TiO₂ nanoparticles was studied for degradation of IC dye (10 and 15 ppm) as a pollutant under the irradiation of visible light. Degradation was performed in self-made reactor under irradiation of 12 lamps of 100 W each. The temperature of the reactor was maintained using air circulating fans. For the photocatalytic experiment, 100 ml aqueous solution of IC dye was taken in a beaker, and 60 mg of catalyst was added to the solution. After adding a catalyst, initially, the solution was stirred in dark for 30 min to attain adsorption–desorption equilibrium between the catalyst and dye solution. After this, the whole setup was brought into the self-made reactor, where photocatalysis reaction was started by irradiation of visible light. During the reaction, 3 to 4 ml of the solution was taken out after an interval of 7 min and centrifuged. The solution was then analyzed using a UV–vis-NIR spectrophotometer (JASCO V-670) at room temperature.

The degradation efficiency was calculated using the following equation:

\[
\text{Percentage degradation} = \left( 1 - \frac{C_t}{C_0} \right) \times 100
\]

(1)

where \(C_0\) and \(C_t\) are the concentrations of Indigo Carmine dye solution at time \(t = 0\) and at time \(t\) respectively.

Moreover, Beer-Lambert law was employed to calculate the concentration of degraded IC solution which is given by:

\[
C = \frac{A}{\varepsilon l}
\]

(2)

where \(A\) is the absorbance detected by graph, \(\varepsilon\) is the molar absorption coefficient, and \(l\) is the optical path length.

**Results and discussion**

**XRD analysis**

The diffraction pattern of prepared TiO₂ is shown in Fig. 1. This XRD pattern shows high intensity peak (110) at 25.3°, which confirms the formation of crystalline anatase...
phase of TiO$_2$ (PDF NO. 01–275-2545) with tetragonal crystal structure and having primitive lattice with lattice parameter $a = 3.79900 \text{ Å}$ and $c = 9.50900 \text{ Å}$. It is also observed that the intensity of the XRD peaks increases with pH and it is maximum for pH 5.

The other XRD peaks at 37.90, 48.04, 54.17, 55.18, 62.78, 69.56, and 75.45 correspond to (004), (200), (105), (211), (204), (215), and (116) planes of anatase phase of TiO$_2$ [26, 27]. It is confirmed that the crystallites size of TiO$_2$ is found to grow with an increase in pH value.

The crystalline size of the prepared powder has been calculated by the Debye Scherrer formula and depicted in Table 1.

$$D = \frac{k\lambda}{\beta\cos \theta}$$  \hspace{1cm} (3)

where $\beta = (FWHM) \times (\pi/180)$ is the broadening ( $\beta = 0.02390$ is the value of prepared sample) at half of the maximum intensity (FWHM), after subtracting instrumental line broadening in radian, $\lambda$ is the X-ray wavelength of the incident radiation (the crystallinity of prepared NTO was analyzed by X-ray diffractometer using Cu-K$\alpha$ radiation of wavelength 1.5060 Å), $\theta$ is Bragg’s diffraction angle, and $K=0.9$ is the dimensionless shape factor, called Scherrer’s constant.

From Table 1, it is observed that the size of TiO$_2$ crystallites increases with an increase in pH of the solution [28].

### Raman spectra

Figure 2 illustrates the Raman spectra of the samples heat-treated at 350 $^\circ$C for 2 h. The observed Raman peaks correspond to the anatase phase of TiO$_2$. In the anatase phase of TiO$_2$, six active Raman modes (3E$_{g}$ + 2B$_{1g}$ + A$_{1g}$) are observed. For all samples, the peaks at 144 cm$^{-1}$ (E$_{g}$), 197 cm$^{-1}$ (E$_{g}$), 399 cm$^{-1}$ (B$_{1g}$), 517 cm$^{-1}$ (A$_{1g}$ + B$_{1g}$), and 639 cm$^{-1}$ (E$_{g}$) are very well matched with the reported data [29]. It is observed that the intensity of Raman peaks decreases with the pH of the solution. The band at 517 cm$^{-1}$ is due to the stretching of Ti-O type vibrations; hence, it shows two Raman modes [30]. Although the samples were prepared by maintaining different pH, no change in the peak position is observed which confirms the absence of impurity in all the prepared samples.

### Morphology of TiO$_2$

Figure 3(a, b, and c) depicts the SEM images of TiO$_2$ nanoparticles prepared at different pH (1, 3, and 5) and heat-treated at 350 $^\circ$C for 2 h. Figure 3(a) shows the SEM image of p1_350. From the figure, the smaller size of TiO$_2$ particles was observed. The agglomeration was also seen in the SEM image due to the smaller size of the nanoparticle. Figure 3(b) and (c) are SEM images of p3_350 and p5_350 which are less agglomerated compared to p1_350 which may be due to the larger size of crystallites. The observed results show that the size of TiO$_2$ crystallites increases with pH which is supported by XRD data.

### TEM analysis

Figure 4(a) shows the TEM image of sample p1_350. It is observed from the TEM image that the prepared TiO$_2$

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**Table 1** Crystalline size of TiO$_2$

| Sr. no | Sample ID | Crystalline size (nm) |
|-------|-----------|-----------------------|
| 1     | p1_350   | 4.8 nm                |
| 2     | p3_350   | 6.5 nm                |
| 3     | p5_350   | 7.0 nm                |
nanoparticles have non-homogeneous distribution and the average size of the TiO$_2$ nanoparticles is found to be 7 nm. Figure 4(b) shows the SAED pattern of p1_350, which confirms the prepared powder is crystalline in nature and it comprises the anatase phase of TiO$_2$. In the SAED pattern, rings are assigned to (110), (004), and (200) planes of anatase TiO$_2$ which are in good agreement with the XRD results. The lattice spacing between the lattice plane was found to be 0.34 nm which corresponds to (110) plane of anatase TiO$_2$ (Fig. 4c). The presence of Ti and O in the synthesized material is confirmed by EDS spectra (Fig. 4d).

Absorption spectra

Absorption spectra of synthesized TiO$_2$ powder are shown in Fig. 5. From this spectrum, it is observed that cutoff wavelength shifts to the higher wavelength with an increase in pH. The shift in absorption edge towards a longer wavelength may be due to an increase in particle size of TiO$_2$ [31].

The optical energy bandgap of prepared samples was calculated by Tauc plot using equation

$$(ahv)^n = A(hv - E_g)$$

(4)
where $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy, $A$ is the constant depend on the material, $n$ is the value which is related to the transition ($n = 2$ for direct bandgap, $2/3$ for direct forbidden bandgap, and $1/2$ for indirect bandgap).

The plot of $(a\nu)^2$ vs $h\nu$, i.e., Tauc plot (Fig. 6), gives direct bandgap energy. The obtained direct bandgap energy of samples was calculated by extrapolating to $h\nu$ axis, i.e., to $\alpha = 0$ and depicted in Table 2 [32]. From this table, it is observed that the energy bandgap decreases with an increase in pH. This decrease in the energy bandgap of TiO$_2$ may be due to an increase in the crystalline size of TiO$_2$ nanoparticles which is also supported by XRD results. The bandgap of semiconductor is size-dependent, hence decrease in bandgap by increasing pH of solution related to increase in crystalline size [8, 33].

**PL spectra of TiO$_2$**

The PL spectra are used to investigate the electronic structure, recombination, and transfer of electron–hole pair in semiconductors [34]. Figure 7 depicts the PL spectra of TiO$_2$ excited at 300 nm. The PL spectra were recorded at room temperature in the wavelength range 320 to 550 nm. It is observed from the spectra that the sample with pH = 1 (p1_350) shows very less intensity peak due to less recombination of electron–hole pairs. As the pH value of the solution increases to 3, the PL intensity is found to increase. This increase in intensity is due to more recombination of
electrons and holes. For sample p5_350, the intensity is intermediate to that of the p1_350 and p3_350 samples. Observed peaks in PL spectra of TiO$_2$ are may be due to self-trapped excitons, oxygen vacancy, and surface defects [29, 35–37]. The band edge emission of 382 nm may be due to recombination of excitons [38]. The peak observed at 397 nm for all samples is due to the indirect transition $\Gamma_{1b} \rightarrow X_{2b}$, and the blue emission peak was found at 450 nm [39–41]. The peak at 468 nm is due to the electron trapped from defect level and oxygen vacancy [42]. The peaks on the higher wavelength side, i.e., at 482 nm and 494 nm are due to oxygen vacancy and transition from Ti$^{3+}$ to TiO$_6^{2-}$ [40]. The lower PL intensity for sample p1_350 due to decrease recombination of charge carriers results in improvement of charge separation[43].

**Degradation measurement of IC dye**

It is reviewed that the materials having less recombination rate of electron and hole shows high photocatalytic activity [43]. Since p1_350 shows low PL intensity among all samples, this sample was chosen to degrade the IC dye under visible light irradiation.

The photocatalytic degradation of the Indigo Carmine dye of concentration 10 and 15 ppm was checked by adding 60 mg powder of p1_350. Figure 8(a) and (b) depict the absorption spectra of photodegraded IC suspension over anatase titania nanoparticles. It was found that, when the solution was stirred in dark, there was a small decrease in the intensity of the peak. As it was exposed to visible light, the intensity was decreased very rapidly, and after 21 min of activity, the absorption peak becomes completely flat. IC concentrations throughout the experiment were carried out by observing the intensity of the absorption peak at 611 nm. A decrease in intensity peak at 611 nm was used to determine the degradation efficiency.

The photodegradation efficiency for p1_350 calculated using Eq. (1) is found to be 87.9% and 83.13% for 10 and 15 ppm IC solution respectively over a period of 21 min under visible light irradiation.

Figure 9 shows a graph of IC degradation efficiency v/s irradiation time for 10 ppm IC dye using a standard catalyst (TiO$_2$-P25) and p1_350 catalyst. It is observed from the figure that degradation efficiency was increased with an increase in irradiation time for both the catalyst and after 21 min of visible light irradiation, efficiency was found to be 68.65% and 87.9% for TiO$_2$(P25) and p1_350 respectively. It is also observed that the degradation efficiency is more for our prepared p1_350 catalyst than that of TiO$_2$-P25.

**Optimization of catalyst dose**

Catalyst doses were taken from 0.2 to 0.8 g/l, to investigate the effect of catalyst dose on degradation efficiency. Figure 10 shows the effect of catalyst dose on the degradation efficiency of IC dye. From this figure, it was observed that initially there was an increase in degradation efficiency with an increase in dose (up to 0.6 g/l). With further increase in catalyst dose (> 0.6 g/l), degradation efficiency was found to decrease. The variation in degradation efficiency with
catalyst dose can be understood on the basis of free radicals. With the increase in catalyst dose from 0.2 to 0.6 g/l, active sites on the surface of catalyst increase which amplifies the free radicals result in more oxidation of IC dye. With further increase in catalyst dose beyond 0.6 g/l, the light-shielding effect increases which reduce degradation of IC dye [44]. Thus, an overdose of the catalyst decreases the rate of degradation which results in a decrease in degradation efficiency.

Scavenger trapping test to determine the photocatalytic mechanism

To decode the prime reactive oxygen species (ROS) during the degradation process, scavenger trapping tests were carried out on p1_350 sample under visible light for 10 ppm dye concentration using 60 mg of catalyst. To explore the exact pathway of photocatalytic reaction, 0.1 mmol of quenchers like ammonium oxalate (AO), i-propyl alcohol (IPA), silver nitrate (SN), and benzoquinone (BQ) was added to trap the hole (h+), hydroxyl radical (OH·), electron (e−), and superoxide radicals O2− respectively. The effect of scavengers on degradation efficiency is shown in Fig. 11. A slight reduction in degradation efficiency was observed on the addition of IPA and SN quencher, which confirms that hydroxyl radicals and electrons are contributing very less in photocatalytic degradation. While for AO scavenger about 34% decrease in efficiency was observed which reveals holes (h+) are actively involved in the degradation process but they act as a secondary reactive species. However, the use of BQ shows drastic suppression in degradation efficiency which confirms that the superoxides O2− radicals play a major role in the fast mineralization of dye.
HPLC analysis

Figure 12 displays HPLC chromatograms of IC dye solution before and after degradation. Figure 12(a) exhibits a single intense peak at retention time (Rt) 4.29 min which corresponds to Indigo Carmine dye while Fig. 12(b) shows the chromatogram of degraded product. It was observed that the intensity of peak at Rt 4.29 min was drastically decreased after the photocatalytic reaction. In addition to the peak of Indigo Carmine dye, two different peaks were found at Rt 1.88 and 2.08 (Fig. 12b). These additional peaks include compounds of different structures and concentrations which are related to the degradation products of dye.

Determination total organic carbon

Total organic carbon (TOC) analysis was performed to find out the degree of mineralization of the IC dye by TiO$_2$ exposed under visible light irradiation. A maximum 62% TOC removal was obtained after 21 min of visible light irradiation, and during degradation of IC dye, some intermediate compounds like NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$ may also form [45].

Conclusion

TiO$_2$ nanoparticles were synthesized by sol–gel technique and crystallites were grown by optimized heat treatment schedule. The anatase phase of TiO$_2$ was confirmed by the XRD measurement. The anatase phase of TiO$_2$ was also supported by the Raman spectra. The surface morphology and effect of pH on TiO$_2$ nanoparticles were studied by SEM. The average size of TiO$_2$ nanoparticle was calculated from TEM and it was found to be 7 nm. The shift in absorption edge due to an increase in particle size of TiO$_2$ was observed in absorption spectra. PL study was carried out to know the recombination of charge carriers at the excitation. Since the recombination of electron and hole was less in p1_350, it was chosen for dye degradation study. The degradation efficiency was found to be 87.9%. The effect of dose on degradation efficiency was also carried out and it was found to

Fig. 11  Effect of charge-carrier quenchers on IC degradation over p1_350 catalyst. The bars indicate percentage of IC dye degradation after 21 min light irradiation

Fig. 12  HPLC analysis  
(a) IC-dye solution.  
(b) Degraded solution
be maximum for 60 mg. The TOC analysis result shows the removal of TOC by 62% and HPLC analysis confirm the degradation of Indigo Carmine dye.

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**Declarations**

**Competing interests** The authors declare no competing interests.

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