The Structural, Morphological and Optical Studies on Pure and W-Doped TiO$_2$ Nano Particles and Their Photocatalytic Activity

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Abstract: In this work, the effects of Tungsten-doping on the crystal structure, morphology and photocatalytic activity of titanium dioxide nano particles are studied. The pure and tungsten doped TiO$_2$ nanoparticles were synthesized by sol–gel method and calcinated at 600°C for 5 hours. The synthesized products were characterized by X-ray diffraction, Scanning Electron Microscope, Energy Dispersive X-ray Atomic spectrum and UV–Visible spectrophotometer, and Photoluminescence study. X-Ray diffraction pattern of pure TiO$_2$ and 1 weight % W-doped TiO$_2$ nanoparticles confirms the anatase structure and increase in the W-doping changes the phase of TiO$_2$ to rutile. Average crystallite size of synthesized nanoparticles was determined using the Debye–Scherrer formula. The crystallite size obtained from pure TiO$_2$ is in the range from 29 nm to 39 nm and W-doped TiO$_2$ is varied from 28 to 33 nm due to the calcination at 600°C for 5 hours. The Scanning Electronmicrograph shows the agglomerated particles of spherical-like morphology. Pure and W-doped TiO$_2$ nanoparticles were also further characterised by absorption spectral studies. Direct allowed band gap of pure and W-doped TiO$_2$ nanoparticles was studied using UV–Vis spectrophotometer. The photocatalytic activity of pure and W-doped TiO$_2$ nanoparticles was investigated using Reactive RedMSB dye.

Keywords: Nanoparticles, Sol–gel method, Optical absorption, XRD, UV–Visible Spectrophotometer, Scanning Electron Microscope.

I. INTRODUCTION

Now a days, environmental pollution is a major problem which threatens human health and ecosystem. [1–6]. The water pollution is mainly caused by discharging of industrial effluents with organic pollutants and it is increased day by day. But world scientists have reached a solution to eliminate or decrease the impact of these types of pollution. In waste water treatment, semiconducting photo catalyst materials have attracted for many potential applications in the water purification and organic pollutant degradation. Because, Semiconductor photocatalyst creates electron-hole pair (e$^-$/h$^+$) upon light irradiation that could be utilized in initiating oxidation and reduction reactions respectively. Among the various photocatalysts, TiO$_2$ has considerable attention for its efficiency, inexpensive, non-toxic chemically stable and easy availability [7, 8]. TiO$_2$ has a wide range of applications such as catalyst supports, fillers, pigments, decomposition of carbonic acid gas, environmental purification, coatings, dielectric material, biomaterials, photoconductors, solar cells, generation of hydrogen gas, gas sensors, etc. [9, 10]. TiO$_2$ is in three different crystalline phases: rutile, anatase, and brookite. Rutile phase is stable compared to the other two phases which are metastable. Anatase and rutile systems have tetragonal unit cells. The rutile phase possesses two TiO$_2$ molecules per unit cell having lattice constant a=4.5937Å and c=2.9587Å and the anatase phase has four TiO$_2$ molecules per unit cell having lattice constant a=3.7842Å and c=9.5146Å. Generally, TiO$_2$ nano crystal phase has been transformed from anatase to rutile structure when the temperature is increased to above 450°C [11, 12]. Anatase and rutile phases of TiO$_2$ nanocrystals are the two main photocactive polymorphic phases with the band-gap energy of 3.20 and 3.02 eV respectively [13]. Band gap value of the anatase phase is larger that than of the rutile phase. Hence, the rutile phase properties are slightly better than the anatase phase properties in semiconducting performance [14]. Photocatalytic activity of TiO$_2$ can be amended by modifying its structure with metals, which can function as electron traps [15–17]. A lot of work can be done to enhance the photocatalytic activity of TiO$_2$ under visible and UV light by adding metal oxides like RuO$_2$, CrO$_2$ and Fe$_2$O$_3$ [18–21]. Photocatalytic activity of TiO$_2$ can be improved by visible and UV light by mixing with low bandgap semiconductors to forma hetero structure. WO$_3$ is one of the important transition metal oxides which has low band gap energy and also absorbs over a wide range of solar spectrum [22, 23]. Tungsten is the one of the transition elements which is gaining interest from many researchers, because the presence of oxide of tungsten (WO$_3$) in the lattice of titanium dioxide provides an effective separation of photogenerated charge carriers in titanium dioxide and also increases surface acidity. [24, 25] In addition to that, doping by
higher valency cations like tungsten modify the electronic structure of TiO$_2$ resulting in a charge separation efficiency [25]. There are several methods such as sol-precipitation[26], ion-impregnation [27], hydrothermal synthesis[28], sol–gel synthesis[29] to obtain homogeneous doping of W in TiO$_2$. Sol-gel is the most simple and sophisticated method proposed by Byun et.al. [30] among the various methods for producing nanoparticles. In this method, synthesis procedure can be carefully and easily controlled. In this work, the effect of tungsten-doping on the crystal structure, morphology and photocatalytic activity of Titanium dioxide nano particles are studied. With this objective, a study was made to improve the catalytic activity of TiO$_2$ in the visible range, by surface modification using tungsten and the modified catalyst was characterized thoroughly. The photocatalytic activity of the modified catalyst was compared with pure TiO$_2$ for the degradation of Reactive RedM5B and its chemical structure is shown as follows:

![Chemical structure of Reactive RedM5B](Image)

II. EXPERIMENTAL

2.1. MATERIALS

Titanium isopropoxide (Sigma-Aldrich, 97% pure), Sodium Tungstate dihydrate (Merk, 98% pure), Ethanol (Hayman, German, 99.99% pure), Hydroxylamine hydrochloride (Sigma-Aldrich, 99% pure), Reactive RedM5B (Erode scientific Company, India) were used as precursor and are used without any further purification. The Reactive RedM5B is a commercial dye mainly used in textile industries was used in this work. Double distilled water was used for the whole synthesis process.

2.2. Preparation of pure TiO$_2$ and W-doped TiO$_2$ photocatalysts

Pure titanium dioxide nanoparticles and 1wt%, 3wt%, 5wt% W-doped TiO$_2$ nanoparticles were prepared by sol gel method. For the preparation of TiO$_2$ nanoparticles, aqueous solution of titanium (IV) isopropoxide was used as starting material. The sol was prepared by mixing titanium iso propoxide (5ml) with 30 ml of Ethanol and dissolved in 1000ml of double distilled water at room temperature. The molar ratio of titanium isopropoxide and alcohol is 1:6 respectively. Hydroxylamine hydrochloride (2 gms) was dissolved in 100ml of deionised water and added gradually to the titanium isopropoxide sol. After stirring, the aqueous solution was centrifuged. The precipitate obtained was dried at 105°C in hot air oven. It was then calcinated at 600°C in a muffle furnace for 5 hours at a constant temperature rise of 2°C/minute. For tungsten doping in TiO$_2$, 1wt % of Sodium tungstate dihydrate solution was added into the TiO$_2$ sol. The mixture of titanium (IV) isopropoxide and Sodium tungstate dihydrate solutions were stirred for 3 hours. After stirring, the aqueous solution was centrifuged, washed, dried and calcined as mentioned above. Similarly 3wt % and 5wt % W-doped TiO$_2$ powders were prepared by the same procedure as mentioned above.

2.3. Physicochemical characterization

X-ray diffraction pattern analysis for pure TiO$_2$ nanoparticles and Ag doped TiO$_2$ powders were recorded by Lab X XRD6000 Shimadzu model with Cu-Ka radiation. The structure and morphology of the nanoparticles were investigated by Scanning Electron Microscopy (SEM) using Jeol JSM 6390 Scanning Microscope. The absorption spectra and optical band gap of the TiO$_2$ nanoparticle samples were measured by using UV-Vis spectrophotometer (Jacso U-670 Spectrometer). The photoluminescence analysis was carried out by using Horiba Jobynvon. The photocatalytic degradation study was carried out by spectrophotometer by using Systronics Model 104.

2.4. Photocatalytic degradation study on Reactive RedM5B

The photocatalytic degradation of sample dye solution can be observed by using spectrophotometer (Systronics Model 104). The $\lambda_{\text{max}}$ of Reactive RedM5B dye was found to be 540 nm. In this work, photocatalytic degradation experiment was carried out with 100 ml aqueous 10, 20, 30 ppm of Reactive RedM5B solution. The solution was taken in a 250 ml Borosil beaker containing 100 mg of TiO$_2$ nanoparticles catalyst calcinated at 600°C at different pH values. This mixture was aerated for 30 min to reach adsorption equilibrium. Then, the mixture was placed nearer to the UV light source at a distance of 25cm away from the beaker. The progress of the photocatalytic reaction can be determined for 30ppm solution at different pH values. The supernatant dye solution was obtained by centrifuging at 5000 rpm for 5 min to separate the photocatalyst and it was used to find the absorbance. The values of the degradation percentage were found to be maximum at pH=3.5. Therefore pH 3.5 was used for the degradation of Reactive RedM5B dye solution [31]. The same procedure was followed for 10ppm, 20ppm and 30ppm solutions and 1wt%, 3 wt % and 5 wt % W-doped TiO$_2$ nanoparticles calcinated at 600°C for 5 hours while the catalyst was used at the pH of 3.5. The percentage of decolorisation was calculated from the differences between initial and final absorbance values using the following equation:

$$\% \text{ of Decolourisation} = \frac{\text{Initial OD} - \text{Final OD}}{\text{Initial OD}} \times 100$$
III. RESULTS AND DISCUSSION

3.1. X-ray diffraction (XRD) analysis

X-Ray Diffraction analysis was used to determine the crystalline structure and phase of the synthesised nanoparticles. Figure 1(a-d) shows the X-Ray Diffraction patterns of pure and W-doped TiO₂ nanoparticles. The results show that most of the peaks to pure TiO₂ and 1wt% W-doped TiO₂ nanoparticles calculated at 600°C confirms the formation of anatase phase by the existence of strong diffraction peaks at 2θ values of 25.3°, 38.44°, 48°, 54°, 55.07°, 63°, 69.23°, 70.89°, and 75.38° corresponding to the crystal planes of (101), (112), (200) (204), (116), (220), and (215), respectively [JCPDS card no 21-1272] belonging to the tetragonal structure. The XRD diffraction patterns obtained for 3 wt % and 5 wt % W-doped TiO₂ nanoparticles are shown in the Figure 1(b-d). XRD patterns of 3 wt % and 5 wt % of W-doped TiO₂ showed the presence of characteristic rutile peaks at 2θ values of 27.4°, 35.7°, 39.1°, 54.3°, and 64.0° to the crystal planes of (110), (101), (200), (211), and (002) respectively (JCPDS card No 88-1175) being a mix of anatase and rutile phases. The fineness of peaks indicates that the nanosized materials were well crystallized. Several studies reported [32, 33, 34] that sol–gel sample of TiO₂ should undergo a phase transformation from anatase to rutile during the higher calcination (above 500°C) temperature in general. Here, the results showed that major phase transformation from anatase to rutile takes place with the increase of wt% of WO₃, new peaks appeared at 2θ =20.45° and 22.83° (marked as W), for the W-doped TiO₂. The new peaks may be attributable to a new component of WₓTi₁₋ₓO₂. It has been observed by other researchers that, high wt % of tungsten doping (5 wt %), retarded the phase transformation (up to 900°C) [35, 36]. But in our experiment did not find any retardant at the current level of doping (3% and 5wt %) [37] suggested that W ions in TiO₂ can either replace titanium ions to form W–O–Ti bonds or locate at interstitial sites.

The average particle sizes of pure TiO₂ powder is approximately 34 nm. The average particle size of 1, 3, and 5wt % W-doped TiO₂ powders are about 28, 34 and 33 nm respectively. The average particle sizes was calculated using the full-width at half maximum measurement at 2θ of the maximum diffraction peaks using Debye-Scherrer’s formula (1),

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

(1)

In this equation, D is the crystallite size, K the Scherrer constant usually taken as 0.89, λ the wavelength of the X-ray radiation (0.15418nm for Cu Kα). Comparing the XRD patterns of pure and W-TiO₂, it appears that W loading does not influence the crystalline structure of TiO₂.

3.2. Scanning electron microscopy (SEM) studies

The SEM images of pure and W-doped TiO₂ calcinated at 600° C are shown in Figure 2 (a-d). From the images,
it can be confirmed that the average agglomerated particle size of pure TiO$_2$ is 34 nm with nearly spherical and homogeneous particles. SEM micrograph of W-doped TiO$_2$ nanoparticles shows that the surface morphology of the particles is nearly spherical with uniform sized particles and coherent together. However, the individual spherical particles are clearly seen due to the nano-clusters formed during the growth. It can be seen that the average agglomerated particle size of 1, 3 and 5 wt% W-doped TiO$_2$ prepared by sol–gel method has little influence on the particle.

![SEM micrographs](image)

**Fig. 2.** (a-d) SEM micrographs of (a) undoped TiO$_2$, (b) 1 wt% W-doped TiO$_2$, (c) 3 wt% W-doped TiO$_2$, and (d) 5 wt% W-doped TiO$_2$.

3.3. Energy dispersive X-ray (EDX) analysis

Analysis of EDX is used to analyze the chemical composition of the prepared material. Figure 3(a) represents the EDX of pure TiO$_2$ nanoparticles prepared by sol-gel method which contains the peaks of titanium and oxygen only. So, it is clear that TiO$_2$ is in pure form and free from any observable impurities. Similarly, Figure 3(b) also shows the EDX of 1, 3 and 5 wt% W-doped TiO$_2$ samples, prepared by sol-gel method. EDX shows only peaks of titanium, tungsten and oxygen elements. From the figure, it is clear that W-doped TiO$_2$ is free from impurities.

![EDX Analysis](image)

**Fig. 3.** EDX Analysis: (a) undoped TiO$_2$ and (b) W-doped TiO$_2$.

3.4. UV-Vis absorption spectroscopy
UV-Visible spectroscopy measurement was performed to measure the absorbance and band gap of pure and 1, 3 and 5wt% W-doped TiO₂ nanoparticles. The optical absorbance spectra of pure and W-doped TiO₂ samples recorded by a UV–Vis spectrophotometer in the range of 200–800 nm are shown in figure 4. It can be seen from the figure that the intensive absorptions are present in the range of below 400 nm. The strong absorption below 400 nm for all the samples shows that, ligand to metal transfer transition O²⁻ to TiO²⁺ takes place [36]. All the UV absorption spectral data of pure TiO₂ show a strong peak at 349 nm. From the figure 4, it is observed that the absorption is shifted towards the longer wavelength side for W-doped TiO₂ samples due to bathochromic shift in optical energy gap.

![Fig. 4. UV-Vis absorbance spectra of undoped, 1, 3 and 5wt% W-doped TiO₂.](image)

The direct band gap energy can be estimated from a plot of (αhν)² versus photon energy (hν). The energy band gap was determined by using the relationship:

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

where \( h \nu = \) photon energy, \( A = \) absorption coefficient ( \( A = 4 \pi k/\lambda \), \( k \) is the absorption index or absorbance, \( \lambda \) is the wavelength in nm), \( E_g = \) energy band gap, \( A = \) constant, and \( n = 1/2 \) for the allowed direct band gap. The value of band gap was determined by extrapolating the straight line portion of \( (\alpha h \nu)^2 = 0 \) on the X axis. The direct band gap energy can be determined from a plot of \( (\alpha h \nu)^2 \) versus photon energy (hν). The intercept of the tangent to the plot will give a good approximation of the direct band gap energies of the samples as given in Figures 5(a) and 5(b) (also called a Tauc plot) [38,39]. The band gap energy of pure, 1wt%, 3wt%, and 5wt% W-doped TiO₂ nanoparticles calculated at 600°C is 2.98 eV, 2.80 eV, 2.60 eV and 2.40 eV respectively. The band gap decreases from 2.80 to 2.40 eV for the W-doped TiO₂ nanoparticles.

![Fig. 5. UV-Vis absorbance spectra and band gap:(a) Undoped TiO₂ (b) 1wt%, 3wt% and 5wt% W-doped TiO₂.](image)

3.5. Photoluminescence (PL) studies

Photoluminescence spectroscopy (PL) is a useful method for finding the electronic structure of nanomaterials, which also gives the information about the transfer behavior of the photo-excited electron–hole pairs in semiconductors, and the rate of recombination [40]. The excitation wavelength of the pure TiO₂ is found to be at 325 nm. Using this wavelength, the band gap of the pure TiO₂ is obtained as 2.98 eV. Similarly, excitation wavelengths of W-doped TiO₂ nanoparticles were observed at 330, 340 and 410 nm. Hence, the band gap values of 1wt%, 3wt% and 5wt% W-doped TiO₂ nanoparticles were changed to 2.80 eV, 2.60 eV and 2.40 eV. Figure 6 shows the photoluminescence spectrum of pure and 1 wt%, 3 wt% and 5 wt% W-doped TiO₂ nanoparticles which show that the position of the peaks is almost similar except the 5wt% W-doped TiO₂ nanoparticles. But the photoluminescence spectra of pure TiO₂ is greater than the PL intensity of 1 wt%, 3 wt% and 5 wt% W-doped TiO₂, which is due to a lower recombination rate of electrons and holes (41–43) in the presence of light irradiation. It indicates that the recombination of charge carriers is effectively reduced by the doping tungsten metal [44]. The results also indicate that the position of Photoluminescence peaks for the doped TiO₂ shift to red direction and also this shift of emission peak towards longer wavelengths.
further supports the lowering of the band gap of TiO$_2$ due to the tungsten doping treatment.

3.6. Photocatalytic decolorisation studies

More number of studies have been done already by the metal doped TiO$_2$ photocatalyst for the degradation of Azo dyes [45-47]. In this experiment, TiO$_2$ has been coupled with semiconductor WO$_3$ for the photocatalytic degradation of Reactive Red M5B. The decolourisation takes place in the absence of the catalyst also, but it is very slow. The experiments were carried out under identical conditions in the presence of UV light for 10ppm, 20ppm, 30ppm of pure TiO$_2$ nanoparticles. Similar studies were conducted for 1 wt %, 3 wt %, 5 wt % W doped TiO$_2$ and presented in the figure 7 (a-d).

Photocatalytic activity for TiO$_2$ and W-doped TiO$_2$ were obtained by measuring decomposition rate of Reactive Red M5B dye aqueous solution under ultra violet radiation. In this investigation Pure TiO$_2$ synthesised by the sol-gel method was taken as a reference. It is observed that, under UV irradiation, the colour removal efficiency in terms of percentage of the initial dye concentration decreased with increase in the initial concentration of the dye. Influence of the catalyst is observed for azo dyes[31]. Photocatalytic activity of pure and W-doped TiO$_2$ under ultraviolet light and removal efficiency of 10ppm, 20ppm, 30ppm Reactive Red M5B upto 210 minutes are shown in the figure 7(a-d).

Fig. 6. Photoluminescence spectrum of undoped, 1, 3 and 5wt% W-doped TiO$_2$.

The highest photoactivity was observed for the 5 wt %W-doped TiO$_2$. After 210 minutes irradiation of aqueous suspension initially containing 10 ppm of Reactive Red M5B, 92% was degraded. The figure 7(a-d) clearly shows the decolourisation of dye solution can be enhanced by the doping of W with TiO$_2$ nanoparticles. This may be explained as follows:

The process of recombination of photogenerated electrons and holes is very important factor for the photocatalytic activity in the semiconductor catalysts. When tungsten doped TiO$_2$ acts as a photocatalyst, photo excitation process takes place by photogenerated holes transfer from the WO$_3$ (valence band) to the TiO$_2$ (valence band) and also photogenerated electrons can transfer from TiO$_2$ (conduction band) to the WO$_3$ (conduction band) [48,49]. Tungsten doping of the TiO$_2$ sample can shift the light absorption near the wavelength of UV to the wavelength of visible range which results in
suppressing the recombination of the excited electrons and holes. This above process results in photogenerated carriers which could be effectively separated. This process results in the W-doped TiO$_2$ photocatalyst to show higher photocatalytic activity than that of the pure TiO$_2$.

IV. CONCLUSION

TiO$_2$ nano particles and 1 wt %, 3 wt %, 5 wt % W-doped TiO$_2$ nanoparticles were successfully synthesized by sol-gel method. The prepared nanoparticles are calcinated at 600°C for 5 hours. According to the XRD pattern, the pure TiO$_2$ and 1 wt % W-doped TiO$_2$ were in anatase crystalline form and it may be due the smaller amount of W in TiO$_2$ which does not affect the crystalline structure whereas 3 wt % and 5 wt % W-doped TiO$_2$ is found to have rutile crystalline structure which confirms the phase transformation due to the Tungsten doping. The average particle size of pure TiO$_2$ powder is approximately 34 nm. The average particle size of 1, 3, and 5 wt % W-doped TiO$_2$ powders are about 28, 34 and 33 nm respectively. SEM images of pure, 1 wt % 3 wt % and 5 wt % W-doped TiO$_2$ confirm the spherical structure with uniform sized particles and are coherent. EDX analysis shows that no impurities are present in the prepared pure TiO$_2$ and W-doped samples. Photoluminescence study indicates that the strong emission peaks obtained from 350 to 400nm confirm the direct recombination between electrons in the conduction band and holes in the valence band and also there is a decrease of intensity in the suppression of electron-hole recombination by the dopant tungsten. Photocatalytic activity of pure and W-doped TiO$_2$ nanoparticles for Reactive RedM5B dye clearly shows the role of W dopants for the enhancement of TiO$_2$ photocatalytic activity under UV light irradiation.

REFERENCES


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