

## Synthesis and studies on photochromic properties of vanadium doped TiO<sub>2</sub> nanoparticles

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### ABSTRACT

Pure and (0.5–3 at%) vanadium doped TiO<sub>2</sub> nanoparticles have been synthesized by wet chemical method. The as synthesized materials have been characterized by using XRD, atomic force microscope (AFM), Raman, EPR and UV–vis spectroscopy techniques. From XRD studies, both pure as well as vanadium doped TiO<sub>2</sub> have been found to show pure anatase phase. The value of lattice constant *c* is smaller in doped TiO<sub>2</sub> as compared to undoped and has been found to decrease with increase in vanadium concentration. AFM studies show formation of spherical particles with particle size ~23 nm in all the samples. Photochromic behavior of these materials has been studied by making their films in alkyd resin. Vanadium doped TiO<sub>2</sub> films show reversible change in color from beige–yellow to brownish violet on exposure to UV light. The mechanism of coloration and bleaching process has been discussed.

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### 1. Introduction

Inorganic photochromic materials have attracted attention of scientific community in recent years due to their promising applications in many areas such as display, imaging, smart window, solar energy conversion and camouflage [1,2]. Various transition metal oxides, such as MoO<sub>3</sub>, WO<sub>3</sub>, TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, etc., show color changes on exposure to either sunlight or UV radiation. It is now well understood that the photochromic phenomena in transition metal oxides is governed by the redox process arising due to optically excited electron–hole pairs [3,4]. However, the main problem lies with slow redox process in them since the process of photo-absorption is much slower as compared to the rate of electron–hole pair recombination [5,6]. The photochromic behavior thus can be enhanced by improving the dynamics of redox process. This can be achieved by using various techniques such as surface modification by rare earth metals [7], doping with other transition metal elements [8], making composite with organic–inorganic materials [9,10], etc.

Among different metal oxides, the transition metal doped anatase TiO<sub>2</sub> is considered to be a prominent photochromic material owing to its wide indirect band gap energy ~3.2 eV [11]. Its other important attributes, viz. long-term stability against photo-chemical corrosion, biological and chemical inertness together with cost effectiveness also make it highly attractive material [12]. TiO<sub>2</sub> doped with several transition metal ions including Co, Cr, Cu,

Mn, Fe, Ni, etc., have been reported to show photochromic effect [13]. Karvinen [14] has studied the effect of trace element (Cr, Fe, Nb, P, Si, V, Mo and Zn) doping on the optical properties of nano-structured TiO<sub>2</sub>. Among these dopants, vanadium (V) has been found to be the most effective in rendering TiO<sub>2</sub> photochromic. Further, it is also reported that reduction of particle size into nanometer range with high surface area and enhanced band gap causes generation of more free or trapped charge carriers and thus resulting into slow rate of electron–hole recombination in these materials to improve the photochromic efficiency [3,15]. Thus, TiO<sub>2</sub> nanoparticles doped with various metal ions, particularly with vanadium hold promise to be very efficient photochromic materials.

Although various physical and chemical methods have been reported for synthesis of V-doped TiO<sub>2</sub> nanoparticles [16–18] however, the focus of most of these studies are related to their photocatalytic activity and particularly about degradation of organic compounds and dyes [19–21]. However, it is quite surprising that there are no systematic studies related to photochromic behavior of V<sup>5+</sup> doped TiO<sub>2</sub>. In this paper we report synthesis of V<sup>5+</sup> doped TiO<sub>2</sub> nanoparticles by wet chemical method and studies on their photochromic behavior together with mechanism of coloration and bleaching in these materials.

### 2. Experimental

#### 2.1. Synthesis of undoped and V<sup>5+</sup> doped TiO<sub>2</sub> nanoparticles

Vanadium doped TiO<sub>2</sub> nanoparticles were synthesized through alkaline hydrolysis of the metal (Ti and V) salt solution followed by its boiling at ~100 °C for 6 h. In a typical synthesis 50 ml of

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1 M  $\text{TiOCl}_2$  was mixed with pre-determined quantity (0.5–3 at%) of sodium metavanadate solution and homogenized by magnetic stirrer for 1 h. pH of the solution was maintained  $\sim 12$ , by addition of 25% ammonia solution ( $\text{NH}_4\text{OH}$ ). The resulting solution was then boiled at  $\sim 100^\circ\text{C}$  for 6 h to obtain yellow precipitate. The precipitate was filtered and washed thoroughly with hot distilled water to remove un-reacted salts and was finally dried at room temperature.

## 2.2. Characterization

The structural characterization of the samples was carried out by powder X-ray diffraction method performed on a Philips X'Pert Pro system by using  $\text{Cu K}\alpha_1$  ( $\lambda = 1.540 \text{ \AA}$ ) radiation. The phase identification was made with the help of standard JCPDS database. Imaging of the sample was carried out by using NT-MDT Solver PRO Atomic Force Microscope (AFM) in tapping mode. For AFM imaging, the powder samples were dispersed in water and spray coated on a freshly cleaved mica surface by using a fine atomizer. The UV–vis diffuse reflectance spectra (DRS) are recorded in the range of 350–1000 nm on pressed pallets of these powder samples by using PerkinElmer Lambda 900 UV–vis Spectrophotometer.  $\text{BaSO}_4$  was used as a reference sample. Raman spectra of the powder samples were recorded on an Avalon Raman Microscope R3-532 using argon ion laser ( $\lambda = 532 \text{ nm}$ ) in the range of 200–1200  $\text{cm}^{-1}$ . X-band EPR spectra were recorded using Bruker EMX 1444 EPR spectrometer operating at 9.455 GHz (fitted with a quartz Dewar for measurements at 120 K). The EPR spectra were calibrated with diphenylpicrylhydrazyl, DPPH ( $g = 2.0037$ ).

## 2.3. Preparation of $\text{TiO}_2$ -alkyd resin films

Films of these materials were prepared in alkyd resin of 40% solid content. In a typical preparation, 1.75 g of doped  $\text{TiO}_2$  powder was mixed with 20 g of alkyd resin and ball milled for 6 h. Approximately 100  $\mu\text{m}$  thick films were prepared for each of the 5 samples by using brush painting on aluminum plate.

## 2.4. Photochromic activity

Photochromic experiments were carried out using an 8 W UV lamp as the light source having wavelength of 365 nm. The samples were irradiated with an intensity of 315 lx. Diffuse reflectance spectra were recorded at regular intervals of time to monitor the coloration and bleaching process.

## 3. Results and discussion

### 3.1. XRD and AFM

Fig. 1 shows the XRD spectra of both undoped and  $\text{V}^{5+}$  (0.5–3 at%) doped  $\text{TiO}_2$  samples. The diffraction peaks of all the samples are indexed to (1 0 1), (0 0 4), (2 0 0), (1 0 5) and (2 1 1) planes of anatase phase of  $\text{TiO}_2$ . Broad XRD peaks indicate formation of nanosized particles of  $\text{TiO}_2$  and their average particle size have been estimated  $\sim 25 \text{ nm}$  by using Debye–Scheerer equation. Formation of spherical particles has been observed from AFM studies for all samples (Fig. 2). AFM image of one of the representative sample (1 at% V), shows particle diameter  $\sim 23 \text{ nm}$ , which is fairly in agreement with XRD results. Similar morphology has also been observed for all other vanadium doped samples. Moreover, comparing these images with undoped  $\text{TiO}_2$ , we found that there is no change in morphology when  $\text{V}^{5+}$  enters into the  $\text{TiO}_2$  lattice.

The values of lattice parameter 'c' and 'a' for all the samples were calculated from their respective XRD spectra. The plot of values of crystal lattice constant 'c' vs. doping concentrations (Fig. 3(a)) shows that value of the lattice constant decreases with increasing

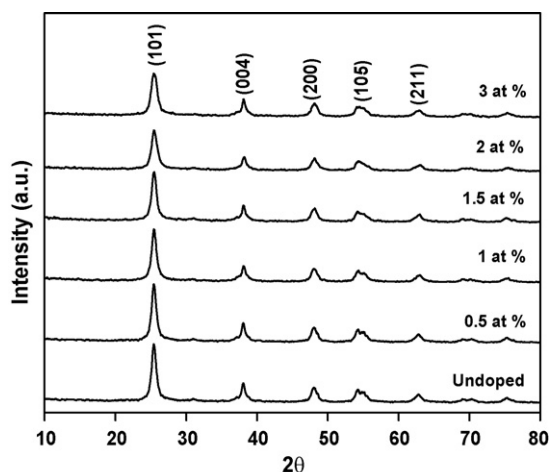


Fig. 1. XRD spectra of undoped and  $\text{V}^{5+}$  doped (0.5–3 at%)  $\text{TiO}_2$  nanoparticles.

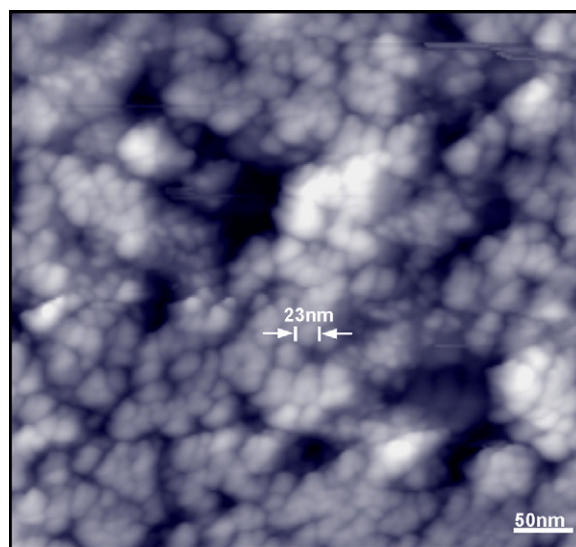


Fig. 2. AFM image of 1 at% vanadium doped  $\text{TiO}_2$  nanoparticles.

concentration of  $\text{V}^{5+}$  dopant ions while lattice constant 'a' values are found relatively unchanged (Fig. 3(b)). The reduction in the value of lattice constant 'c' with increasing concentration of  $\text{V}^{5+}$  may be attributed to the systematic substitution of small  $\text{V}^{5+}$  ions (0.054 nm) at octahedral  $\text{Ti}^{4+}$  sites (0.061 nm), in  $\text{TiO}_2$  lattice [22–24].

### 3.2. UV–vis diffuse reflectance spectroscopy

Optical diffuse reflectance spectra of both undoped and doped  $\text{TiO}_2$  nanoparticles, measured at room temperature are shown in Fig. 4. The undoped  $\text{TiO}_2$  shows sharp absorption at 383 nm, indicating band gap energy of  $\sim 3.26 \text{ eV}$ , corresponding to anatase phase of  $\text{TiO}_2$  [25]. However, doping of vanadium in  $\text{TiO}_2$  results into red shift of absorption edge compared to undoped  $\text{TiO}_2$ . The effect becomes more prominent with increasing vanadium concentration, suggesting decrease in the band gap of  $\text{TiO}_2$  caused by substitution of  $\text{V}^{5+}$  ions at  $\text{Ti}^{4+}$  site. The band gap energy of vanadium doped  $\text{TiO}_2$  samples has been calculated from UV–vis diffuse reflectance spectra. It was found that the band gap energy decreased from 3.26 to 2.85 eV with increase in vanadium doping concentration in  $\text{TiO}_2$  (Table 1). This decrease in band gap energy with the addition of vanadium is attributed to doping of vanadium

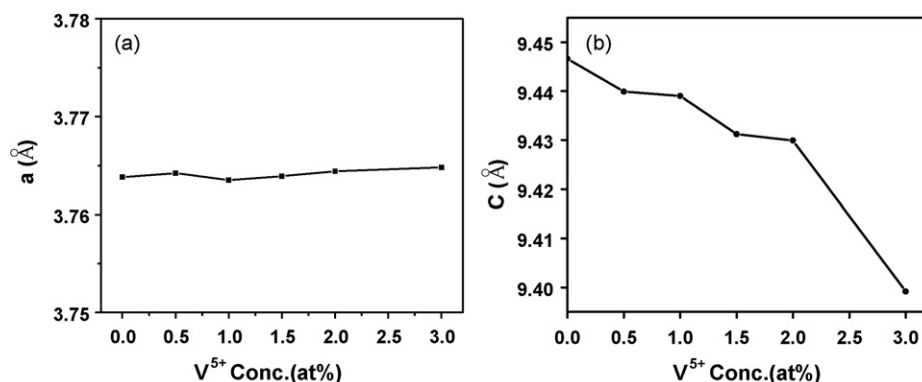


Fig. 3. (a) Variation of lattice constant 'c' vs. vanadium ion concentrations. (b) Variation of lattice constant 'a' vs. vanadium ion concentrations.

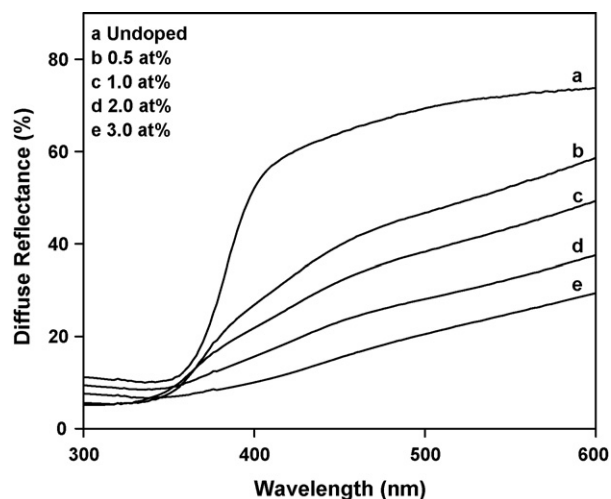


Fig. 4. UV-vis diffuse reflectance spectra of undoped and V<sup>5+</sup> doped (0.5–3 at%) TiO<sub>2</sub> nanoparticles.

ions in TiO<sub>2</sub> lattice [23]. Further, from the diffuse reflectance spectra of the sample it is observed that the reflectance values decrease with the increase in the concentration of V<sup>5+</sup> ions. These observations again suggest doping of V<sup>5+</sup> ions in TiO<sub>2</sub> lattice [26–28] as has been inferred from the XRD studies.

### 3.3. Raman spectroscopy

The photo-reactivity of TiO<sub>2</sub> particle gets affected due to presence of vanadium species on surface of TiO<sub>2</sub> particle [29]. In order to check the presence of vanadium species on TiO<sub>2</sub> surface, Raman spectra of both undoped and 1 at% V<sup>5+</sup> doped TiO<sub>2</sub> nanoparticles were recorded (Fig. 5). Similar spectra have been observed for all vanadium-doped samples. The appearance of three characteristic absorption modes at 401, 519 and 640 cm<sup>-1</sup> are due to B<sub>1g</sub>, A<sub>1g</sub> and E<sub>g</sub> phonon modes of anatase TiO<sub>2</sub> phase respectively [30]. The absence of any weak narrow band at ~1046 cm<sup>-1</sup> due to V=O

Table 1  
Band gap energy estimated from the diffuse reflectance spectra.

S. No.	V <sup>5+</sup> concentration (at%)	Band gap <sup>a</sup> (eV)
1.	0.0	3.26
2.	0.5	3.15
3.	1.0	3.03
4.	2.0	2.90
5.	3.0	2.85

<sup>a</sup> Band gap was calculated by UV-vis diffuse reflectance spectra.

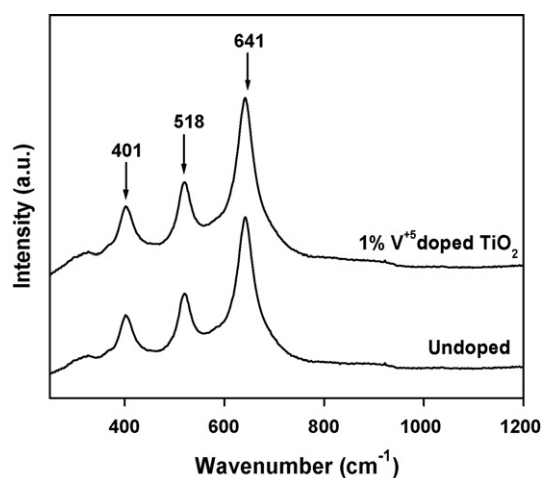


Fig. 5. Raman spectra of undoped and 1 at% V<sup>5+</sup> doped TiO<sub>2</sub> nanoparticles.

stretching vibration or at 907 and 938 cm<sup>-1</sup> of isolated surface vanadyl or metavanadate species ruled out the possibility of the presence of any vanadium species at the surface of TiO<sub>2</sub> [31]. The studies therefore suggest that the wet chemical method used in the present studies provides a simple means of synthesizing V<sup>5+</sup> doped TiO<sub>2</sub> particles.

### 3.4. Photochromic studies

Photochromic behavior of undoped and doped composite films was studied by exposing them to UV light of 315 lx intensity for 30 min. All doped films show reversible color change from beige-yellow to brownish-violet (Fig. 6) whereas, no change in the color of the film is observed for undoped samples. The relative change in reflectance intensity, i.e. relative diffuse reflectance (RDR) val-

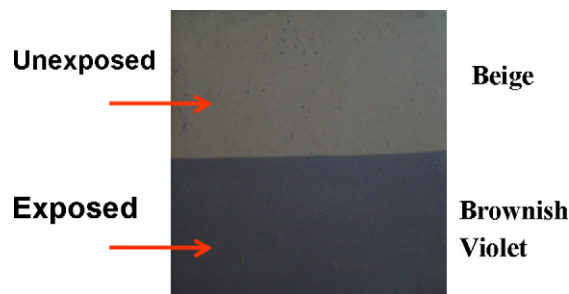


Fig. 6. Photograph of 1 at% vanadium doped TiO<sub>2</sub> composite film showing color change before and after exposure to UV light.

**Table 2**Relative diffuse reflectance (RDR) of vanadium doped (0.5–3 at%) TiO<sub>2</sub> composite films at 750 nm after UV irradiation for 30 min.

S. No.	V <sup>5+</sup> concentration (at%)	Diffuse reflectance (%) at 750 nm		Relative DR <sup>a</sup> (%)	C.E. <sup>b</sup> ( $\eta_{pc} \propto \Delta O.D.$ )
		Original	Colored		
1.	0.5	48.57	35.15	27.63	0.1404
2.	1.0	45.44	28.33	37.65	0.2052
3.	1.5	42.37	32.54	23.17	0.1146
4.	2.0	39.76	34.74	12.62	0.0586
5.	3.0	39.41	36.03	08.57	0.0389

<sup>a</sup> Relative diffuse reflectance.<sup>b</sup> C.E. ( $\eta_{pc}$ ) = coloration efficiency,  $\Delta O.D.$  = change in optical density.

ues for all these films were calculated from the diffuse reflectance spectra recorded before and after exposure to UV-light, are shown in Table 2. It may be noted that 1 at% V<sup>5+</sup> doped TiO<sub>2</sub> composite film shows maximum RDR value as compared to those for the films containing TiO<sub>2</sub> particles with higher concentration of V<sup>5+</sup> ions (>1 at%). Further, we have estimated coloration efficiency ( $\eta_{pc}$ ) of all vanadium doped composite films by using following equation [32] and the data are listed in Table 2

$$\eta_{pc} = \frac{\Delta O.D.}{It} \quad (a)$$

where  $\eta_{pc}$  is the coloration efficiency,  $I$  is the light intensity,  $t$  is the exposure time and  $\Delta O.D.$  is the change in optical density, which is calculated by

$$\Delta O.D. = \log_{10} \left( \frac{R_b}{R_c} \right) \quad (b)$$

where  $R_b$  and  $R_c$  are the reflectance before and after coloration, respectively.

We observed that 1 at% V<sup>5+</sup> doped sample shows maximum coloration efficiency (0.2052) among all doped samples. Therefore, 1 at% vanadium is observed as the optimum concentration to get best photochromic effect in the present samples.

In case of transition metal doped TiO<sub>2</sub>, photoactivity as well as photochromic effect depend on lifetime of photo-generated electron–hole pairs which in turn is highly dependent on the dopant type and their concentration [33]. The doping of transition metal in TiO<sub>2</sub> lattice has been reported to strongly affect the photoactivity up to an optimum concentration in these materials [34]. Further, the electron–hole pair recombination process in doped nanoparticles takes place through tunneling of trapped charge carriers. Thus, the recombination process depends on the separation of e<sup>-</sup>/h<sup>+</sup> trap centers. At lower concentration of dopant ion, due to longer average distance between trap sites the recombination of trapped charge carriers become difficult through the process of tunneling. Therefore, the dopant acts as trap centers rather than

recombination center at lower concentration of doping. While at higher concentration, the average distance between trap centers decreases with increase in the number of dopant confined within a particle resulting higher recombination rate. In the present studies, it was found that, when the V<sup>5+</sup> dopant concentration is more than 1 at% in TiO<sub>2</sub> lattice, the photochromic effect was decreased. This behavior suggests that up to 1 at% vanadium acts as trap centers for optically excited electrons and higher concentration leads to recombination centers for electron–hole pairs.

### 3.5. Photochromic mechanism

In order to understand the mechanism of color change and bleaching process, diffuse reflectance studies were carried out in detail on 1 at% V<sup>5+</sup> doped TiO<sub>2</sub> composite film (Fig. 7). The coloration process of composite film, after 30 min of UV irradiation is shown in Fig. 7(a). The diffuse reflectance (DR) values are found to decrease with increasing exposure time in the visible region. Maximum decrease in DR values was found at 750 nm from ~45 to ~28% with exposure time of 30 min. Similarly, bleaching process of composite film was studied by recording the diffuse reflectance spectra at different intervals by keeping the samples under normal light conditions inside the room (Fig. 7(b)). The bleaching was faster in the beginning and then slowed down with passage of time; up to 60% reversibility was observed after ~20 h and turned back almost to its original color after ~7 days.

The metal ion dopants influence the photo-reactivity of TiO<sub>2</sub> by acting as electron (or hole) trap centre within band gap of TiO<sub>2</sub> and alter the e<sup>-</sup>/h<sup>+</sup> pair recombination rate [35] through following process.

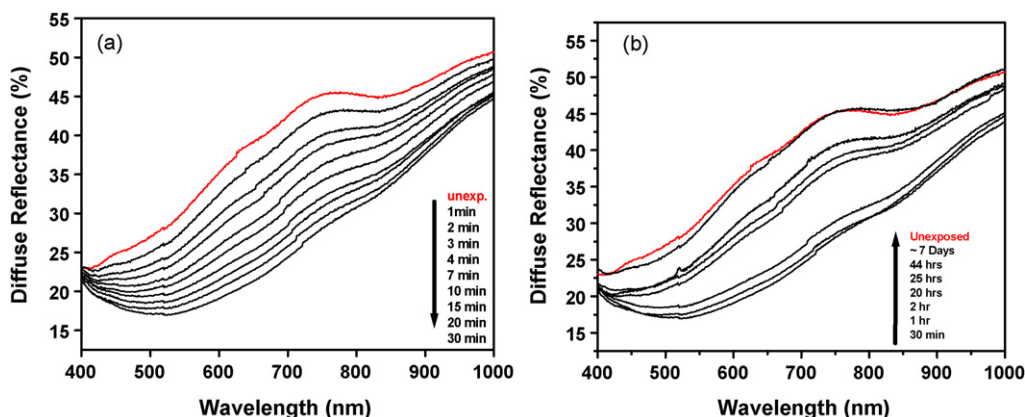
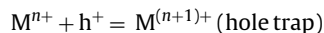
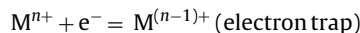


Fig. 7. (a) Coloration process and (b) bleaching process of 1 at% V<sup>5+</sup> doped TiO<sub>2</sub> composite film with the different interval time.

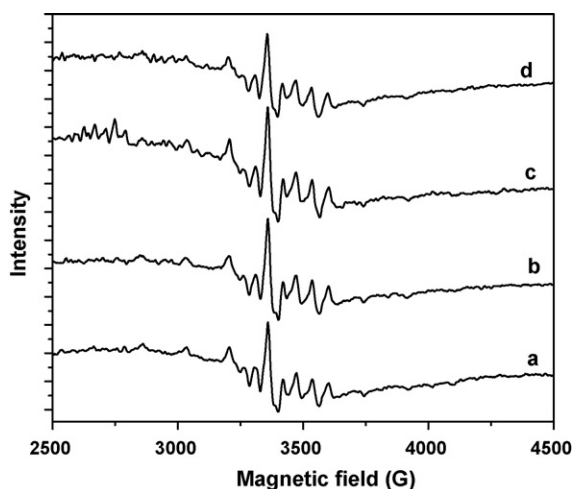
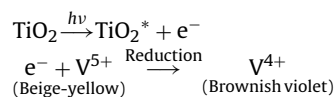
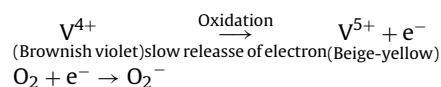


Fig. 8. EPR spectra of 1 at% V doped TiO<sub>2</sub> composite film after exposure (a) 10 min, (b) 20 min, (c) 30 min, and (d) keeping in dark for 24 h.

The energy level of  $M^{n+}/M^{(n-1)+}$  lies below the conduction band edge ( $E_c$ ), whereas energy level of  $M^{n+}/M^{(n+1)+}$  lies above the valence band edge ( $E_v$ ). In the present case, vanadium doping creates energy level just below the conduction band edge of TiO<sub>2</sub> and act as trap centers for photo-generated electrons. When the composite film is exposed to UV light, electron-hole pairs are generated and the excited electrons are trapped at V<sup>5+</sup> trap centers, where V<sup>5+</sup> is reduced to V<sup>4+</sup> state [36] and color change is observed from beige-yellow to brownish-violet. The probable mechanism for coloration process of doped TiO<sub>2</sub> is shown below.



When the light source was removed, V<sup>4+</sup> state oxidized either by slow release of the trap electrons, or trapping by atmospheric oxygen in air to become V<sup>5+</sup> state. The possible bleaching process is shown below.



In order to experimentally verify this redox process, X-band EPR studies are carried out on 1 at% V-doped TiO<sub>2</sub> sample while exposing it for different intervals of time (Fig. 8(a–c)). From this figure, all exposed samples show an EPR signal characteristic for V<sup>4+</sup> ( $s = 1/2, I = 7/2$ ) [31]. Further, the intensity of characteristic EPR signal for V<sup>4+</sup> ions are found to increase with increase in exposure time, which clearly indicates the photo-reduction of V<sup>5+</sup> to V<sup>4+</sup> state. Similarly, as expected the sample kept in dark for ~24 h (Fig. 8(d)) after exposure showed decrease intensity of EPR signal for V<sup>4+</sup> ions. These studies indicate that the coloration and bleaching processes observed are due to transition from V<sup>5+</sup> to V<sup>4+</sup> state and vice versa.

Moreover, in order to understand the role of atmospheric oxygen on bleaching process, two exposed composite films of 1 at% V<sup>5+</sup> doped TiO<sub>2</sub> were taken for diffuse reflectance studies. These films were kept in two different atmospheres, i.e. under normal light conditions in ambient and N<sub>2</sub> atmosphere (99.9% purity) for 5 h. Then, diffuse reflectance spectra were recorded after 5 h (Fig. 9). These spectra indicate bleaching of the color of the film kept under N<sub>2</sub> environment was insignificant as compared to the one which was kept under normal atmospheric condition. This experiment suggests that the bleaching process in the present studies was

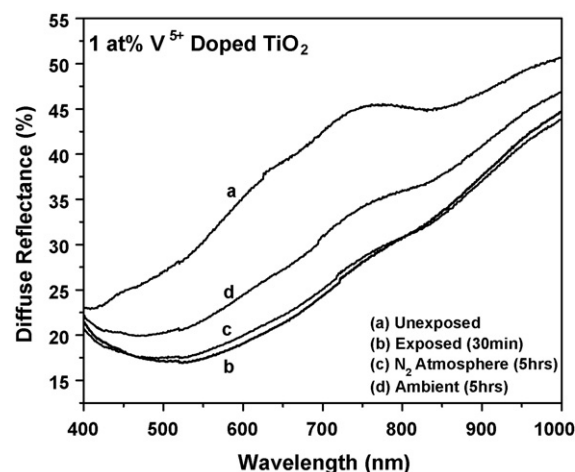


Fig. 9. UV-vis diffuse reflectance spectra of 1 at% V<sup>5+</sup> doped TiO<sub>2</sub> composite film without UV irradiation (a), with UV irradiation for 30 min (b), 5 h in N<sub>2</sub> environment (c), and ambient atmosphere after UV irradiation (d) respectively.

chemical in nature and the trapped electrons were slowly released due to re-oxidation of V<sup>4+</sup> to V<sup>5+</sup> by surface adsorbed atmospheric oxygen resulting in the formation of unstable O<sub>2</sub><sup>-</sup> species [37]. These unstable O<sub>2</sub><sup>-</sup> species release electrons and may recombine with photo-holes to become stable O<sub>2</sub>. Therefore almost original color is returned in film after putting in ambient atmosphere. Similar observation were made on bleaching process of photochromic polyoxometallates containing W<sup>5+</sup> and Mo<sup>5+</sup> by Chen et al. [38], Which shows that oxygen in the air reoxidized W<sup>5+</sup> and Mo<sup>5+</sup> in to Mo<sup>6+</sup>.

#### 4. Conclusions

Synthesized ~23 nm nanoparticles of vanadium doped TiO<sub>2</sub> by wet chemical method. XRD results confirmed the formation of pure anatase phase of TiO<sub>2</sub> in all samples. The lattice constant *c* values have been found to decrease with increasing vanadium ion concentrations indicating incorporation of vanadium ion in TiO<sub>2</sub> lattice. Diffuse reflectance spectra of doped samples show gradual decrease in reflectance values with increase of vanadium ion concentrations, whereas, undoped sample shows maximum reflectance values. The photochromic effect of these materials was studied by making films in alkyd resin. On exposure to UV light, color of the film was found to change from beige to brownish-violet. The maximum photochromic effect was observed in 1 at% V<sup>5+</sup> doped TiO<sub>2</sub> composite film. The coloration process of these films resulted due to trapping of photo-generated electrons at vanadium sites below conduction band edge of TiO<sub>2</sub> and the bleaching process resulted due to release of trapped electrons to atmospheric oxygen.

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