CHAPTER VI

Applications of nanotitania in photocatalytic and photochromic activities
Due to rapidly growing industries and techno-plants in recent years, problems of air and water pollution have emerged as the biggest challenge across the globe. A number of techniques have been developed and adopted in order to overcome the problems one by one. However, each of the remedial method has its own limitation in terms of cost and efficiency. Photocatalysis could be an alternative way to tackle problems under light illumination (natural or artificial). Catalysis deals with the many environmental related aspects, for instance, from the catalytic converter in automobiles to the causes of the ozone hole. Catalysts are the chemical compounds which have capabilities to speed up the chemical reaction without consuming itself. Although less free energy is required to reach the intermediate state, but the total free energy involved from the reactant to the product stage does not change. Many transition metals and transition metal complexes are used in catalysis, e.g., nickel, palladium, platinum etc. out of which some of them are used routinely in food industry, petrochemical industry, pharmaceutical industry, agricultural industry etc. The catalysts are mainly used through hydrogenation reaction. The catalytic reactions are preferred in environment friendly (green route) which could avoid or minimize waste generation [1]. The catalytic water treatment using metals such as Pt and Pd for degrading the environmental contaminants is very expensive. The best known candidate for photocatalysis is titania. In nanoscale form titania has additional advantages along with other conventional properties, which is non-toxic as well as inexpensive. This chapter will focus on the photocatalytic activity of nanoscale titania under UV light illumination using methyl orange (MO) as the target, apart from brief discussion on photochromic response of Ag doped nanotitania system.

### 6.1 Photocatalysis and surface area characterization

Photocatalysis generally requires light energy and catalytically active agents. In
case of titania, photocatalysis occurs only when UV-light is incident on the surface of catalyst. When UV photons strike the catalyst surface, it initiates redox in a systematic manner to help degrading environmentally hazardous species and pollutants.

6.1.1 Bruner-Emmett-Teller (BET) surface area and pore size analysis through $\text{N}_2$ adsorption-desorption study

Surface analysis of nano-dimensional objects is the basis of evaluating the nature of voids, pores and unfilled regions. The analysis of nitrogen isotherm is a standard method for the determination of specific surface area and pore size distribution of porous, solid state object. To investigate the effect of RE ion doping on the pore structure and adsorption capacities of the TiO$_2$ to be used as a nanocatalyst, a series of nitrogen gas ($\text{N}_2$) adsorption/desorption tests were conducted and the experimental results of which are presented in Fig 6.1. The representative isotherms basically represent responses of pure (T2), Eu$^{3+}$ doped (EuT2) and Tb$^{3+}$ doped (TbT3) nanoscale powders. In case of doped titania system, a large hysteresis is attributed to the existence of pore cavities larger than the openings (throats), leading to ink-bottle pores [2]. A hysteretic curve occurs during complete physical process of adsorption/desorption. In this type of hysteresis, the quantity of adsorbed gas when added is different than when it is being removed. The hysteresis loop of type H2 in the IUPAC classification, which is characterized by a steep desorption branch and a smoothly increasing adsorption branch, is associated with the existence of inkbottle-type pores. This type of pores essentially consisting of wide bodies fitted with narrow necks. In the presence of such kind of pores, capillary condensation occurs during adsorption is governed by the radius of curvature of the wide body of the pores, whereas capillary evaporation during desorption, of the capillary condensate in
the pores is obstructed by liquid remaining condensed in the narrow necks (pore blocking) [2]. As a general trend, nitrogen uptake increases with increasing $P/P_o$ value, but with a steeper adsorption and desorption response at a higher range of $P/P_o$ value corresponding to the Tb$^{3+}$ doped nanotitania sample which is due to uniformity in the diameter of the throats [3].

The shape of adsorption and desorption branches in case of Eu$^{3+}$ doped nanotitania, however, is due to the existence of different pore sizes. The isotherms, which appear in the form of closed hysteresis loops, are characterized by varying extent of slanting and with different loop areas. In fact, a hysteretic feature is the indication of different adsorption and desorption rates of N$_2$ molecules within the specimen under study. This is chiefly because of adequate pore-size distribution in the mesostructure region. Apparently, each of the hysteresis loops is more prominent above a relative pressure of magnitude $\sim 0.5$. The hysteretic feature is more steep and open for TbT3 specimen, as compared to both the un-doped and Eu$^{3+}$ doped nanotitania systems. Essentially, this is due to significant difference of adsorption and desorption rates in the former than later.

![Fig. 6.1 N$_2$ adsorption/desorption isotherms of (a) un-doped (T2), (b) Tb$^{3+}$ doped nanotitania (TbT3) samples and (c) Eu$^{3+}$ doped nanotitania (EuT2) samples](image)

Fig. 6.1 N$_2$ adsorption/desorption isotherms of (a) un-doped (T2), (b) Tb$^{3+}$ doped nanotitania (TbT3) samples and (c) Eu$^{3+}$ doped nanotitania (EuT2) samples
The surface area information can be derived from the tail region of the isotherms. The specific surface area is generally calculated from the linear portion of the adsorption isotherm, represented by the Brunauer-Emmet-Teller (BET) equation [4].

\[
\frac{P / P_0}{V_a(1 - P / P_0)} = \frac{1}{V_m \cdot C} + \frac{C - 1}{V_m \cdot C} \left( \frac{P}{P_0} \right) \quad (6.1)
\]

where, \( V_m \) is the quantity of gas adsorbed when the surface is entirely covered with a monolayer, \( V_a \) is the quantity of gas adsorbed at pressure \( P \), and \( C \) is a constant representing the difference of heat of adsorption of the first layer and the heat of liquefaction of the adsorptive material. The specific surface area \( S_{BET} \) of 1 g of the adsorbent is then calculated according to the expression given by

\[
S_{BET} = \frac{V_M \cdot \sigma \cdot N_A}{m \cdot V_O} \quad (6.2)
\]

where, \( m \) is the mass of the sample, and \( \sigma \) is the area of a single N\(_2\) molecule (16.2 \( \times \) \( 10^{-20} \) \( m^2 \)).

Liquid interfaces in porous materials produce a significant pressure depression, which can be used to determine the pore size in nanostructured system. The pores are classified according to their average width (2\( r \)) into free groups: micropores (2\( r \)<2 nm), mesopores (2<2\( r \)<50 nm), and macropores (2\( r \)>50 nm). This classification was based on the relevant adsorption mechanism [5].

The respective BET surface area (\( S_{BET} \)), as for T2, TbT3 and EuT2 specimen, are estimated to be 93.98, 380.45 and 311.24 m\(^2\)/g. The \( S_{BET} \) for TbT3 is \(~4\) fold and for EuT2 is about \( 3.3 \) times higher than its un-doped (T2) counterpart. Similarly, the respective pore volumes corresponding to the T2, TbT3 and EuT2 nanotitania specimens are found as 0.169 cc/g, 0.435 cc/g and 0.322 cc/g. A larger specific
area, as exhibited by the doped sample, can be attributed to the impurity related
defects, mesopores and nanoscale interfaces which are likely to influence the BET
mechanism invariably while slowing down the desorption rate drastically.

The pore size distribution curves are presented in Fig. 6.2. The pore filling, in the
process of condensation, follows the formation of a liquid film on the cavity wall
and thus is controlled by the radius of curvature of the pore cavity, \( r_c \). Essentially,
the pore filling (adsorption) is mediated through capillary condensation while
pore emptying (desorption) occurs through an abrupt evaporation process. The
pressure condensation, \( P_c \) is given by the Kelvin-Laplace equation [6]

\[
\ln \left( \frac{P_c}{P_0} \right) + \frac{2 \gamma_s V_m}{(r_c RT)} = 0 
\]  \hspace{3cm} (6.3a)

Here, \( P_0 \) is the saturated vapor pressure and \( \gamma_s \) is the surface tension of liquid N\(_2\). The parameters \( V_m, r, R \) and \( T \) basically represent molar volume, radius of the
curvature of the cavity, the universal gas constant (8.31 SI units) and working
temperature (77 K); respectively. The evaporation in the process of desorption
occurs after the formation of a hemispherical meniscus in the pore neck and thus
is controlled by the radius of the neck, \( r_n \). The pressure of desorption, \( P_d \) is
determined by the Kelvin-Laplace equation for the equilibrium meniscus in the
cylindrical neck, given by [6]

\[
\ln \left( \frac{P_d}{P_0} \right) + \frac{2 \gamma_s V_m}{(r_c RT)} = 0 
\]  \hspace{3cm} (6.3b)

The pore size \((2r)\) is estimated to be \( \sim 5.2, 3.2 \) and \( 4 \) nm for T2, TbT3 and EuT2
samples; respectively. Interestingly, Tb\(^{3+}\) doped nanotitania specimen exhibits
only weak tailing for pores of size \((2r)\) greater than \( \sim 9 \) nm, whereas un-doped and
Eu\(^{3+}\) doped specimens are characterized by a comparatively long tailing in this
region. Owing to the larger ionic size, the introduction of Eu$^{3+}$ and Tb$^{3+}$ into the host titania lattice might have caused a higher space filling effect. We speculate that, numerous inhomogeneous pores of larger dia are adequately occupied by the dopant ions (ionic radii, Tb$^{3+}$~92 pm, Eu$^{3+}$~94 pm, Ti$^{4+}$~68 pm). In an earlier work, it was shown that the pores of size ~3.1 nm (Bohr exciton diameter of TiO$_2$) could be adequately filled through PbS molecular adsorption [7]. Nevertheless, TbT3 nanotitania has a broad distribution profile, with a peak maxima at ~2.3 nm (2$r$=4.6 nm). A wider full width half maxima (FWHM), offered by TbT3 specimen indicate that, new voids and mesopores of varying sizes are generated by way of inclusion of Tb$^{3+}$ ions into the titania host. This is favorable when Tb$^{3+}$ ions are more likely to occupy interstitial sites than the substitutional sites, and where replacement of Ti$^{4+}$ is not mandatory. However, this was not so for Eu$^{3+}$ doped nanotitania case even though the ionic radii of Eu$^{3+}$ and Tb$^{3+}$ are quite comparable. The BET parameters of the investigated samples are enlisted in Table 6.1.

![Fig. 6.2 Pore size distribution of (a)un-doped (T2), (b)Tb$^{3+}$ doped nanotitania (TbT3) and (c)Eu$^{3+}$ doped nanotitania (EuT2) samples](image-url)
Table 6.1 Textural parameters of titania samples obtained through the BET surface analysis.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( S_{\text{BET}} ) (m(^2)/g)</th>
<th>( V_{\text{tot}} ) (m(^3)/g) ( \times 10^{-6} )</th>
<th>( r ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T2</td>
<td>93.976</td>
<td>0.169</td>
<td>26.2</td>
</tr>
<tr>
<td>TbT3</td>
<td>380.454</td>
<td>0.435</td>
<td>23.6</td>
</tr>
<tr>
<td>EuT2</td>
<td>311.24</td>
<td>0.322</td>
<td>20.0</td>
</tr>
</tbody>
</table>

6.1.2 Analytical techniques employed for exploiting photocatalytic performance of un-doped and doped nanotitania systems

A common target e.g., methyl orange (MO, \( \text{C}_{14}\text{H}_{14}\text{N}_{3}\text{NaO}_{3}\text{S} \)) was chosen for photocatalytic studies. Known for its strong carcinogenic and mutagenic values, researchers across the globe always look for alternative, yet versatile candidates that might degrade this hazardous element in an effective manner. The MO is a pH indicator frequently used in titrations because of it can facilitate clear and distinct colour change. As it changes colour at a pH of the mid strength acid, it is mostly used in titration for acids. It is also employed in dyeing and printing textiles.

The photocatalytic activity of the un-doped and \( \text{Tb}^{3+} \) and \( \text{Eu}^{3+} \) doped nanoparticles were evaluated by observing the degradation of MO dye under UV light illumination. Following an estimation in an earlier work [8], a suspension of 0.25 g/L of the nano-catalyst is added to the MO solution (10 mg/L), followed by a ultrasonic agitation for 15 min and stirring for 1 h. A UV cabinet was employed for photocatalytic studies. The samples were placed at the base of the cabinet and at a distance of 12 cm from the UV source (\( \lambda = 365 \) nm). The measured power at the sample position is approximately, 0.75 \( \mu \text{W/cm}^2 \) (~5 Lux). The catalyst loaded dye solution is then subjected to UV illumination for 15, 30, 45 and 60 min and
followed by high speed centrifugation (~5000 rpm). The residue is discarded and supernatant free from the catalyst is kept ready for subsequent experiments. 5 mL of the solution is taken for the optical absorption studies knowing that the MO solution, without a catalyst, has an initial absorption ($A_0$) located at ~464 nm [9]. The decrease in concentration or degradation of MO from its initial value is analyzed from the strength of reduction of the absorption maxima ($A_t$) of the UV exposed specimen. The percentage of degradation of MO solution can be given by:

$$\% \text{ degradation} = \frac{A_0 - A_t}{A_0} \times 100$$  \hspace{1cm} (6.4)

### 6.2 Photocatalytic activity of un-doped and RE-doped nanotitania systems

The photocatalytic response of the un-doped (T2), Tb$^{3+}$ doped [TbT1 (1% Tb doping), TbT2 (2.5% Tb doping) and TbT3 (5% Tb doping)] and Eu$^{3+}$ doped [EuT1 (1% Eu doping), EuT2 (2.5% Eu doping) and EuT3 (5% Eu doping)] nanotitania system are evaluated by considering MO dye as the targeting agent. The respective absorption responses of the un-doped, Tb$^{3+}$ doped and Eu$^{3+}$ doped nanocatalyst with and without UV-exposure, are depicted in Fig. 6.3 (a), (b) and (c). As shown in Fig. 6.3 (a), in presence of a nanotitania catalyst (T2), the strength of absorption (positioned at ~464 nm) of the MO dye, followed a steady fall with increasing time of UV-exposure. Nonetheless, a lowering of the absorption is more significant in case of use of doped nanotitania catalysts. Moreover, lowering of absorption is highest for the Eu$^{3+}$ doped nanocatalyst. Upon UV light irradiation, the host TiO$_2$ semiconductor would release electrons ($e^-_{CB}$) into the conduction band and holes ($h^+_{VB}$) into the valence band. The charge carrier generated may get trapped in to the Ti$^{4+}$ or, O$^{2-}$ defect sites, or may recombine.
with their counterparts to dissipate energy. On the other hand, the charge carrier would migrate to the nanoparticle surfaces and initiate the redox reaction (oxidation/reduction), thereby converting harmful organic molecules to the harmless entities.

Infact, the high oxidative potential of the holes in the photocatalyst allows the formation of reactive intermediates. The reactive hydroxyl radicals (•OH) can be formed either through decomposition of water, or by the reaction of a hole with OH⁻. The hydroxyl radicals and photogenerated holes are extremely strong non-selective oxidants which could lead to the degradation of MO at the surfaces of the nanoparticles [10]. The recombination event of the photo-generated $e^-h^+$ carriers is generally hindered by the creation of intermediate/defect states within the band gap of the host titania. The oxygen vacancies and un-occupied 4f level of the Tb³⁺ ions normally act as photo-generated electron scavengers, while surface adsorbed OH representing a hole trap [11]. Since the MO target was in aqueous form, the water molecule will come in contact with the catalyst surface and OH group or dissolved O₂ are likely to get adsorbed by different active sites of the catalyst. The oxygen vacancy (with trapped electrons F, F⁺, F²⁺) centers are easily de-trapped and transfer the electrons to the adsorbed oxygen, which in turn produce a superoxide radical, while water and hydroxyl ions are transformed to hydroxyl radicals by the photo-generated holes [12, 13]. These superoxide and hydroxyl radicals being very strong oxidizing agents readily degrade the complete dye to its constituent products [14]. The oxidation and reduction reaction steps involved in photoexcitation, generation of radicals and dye degradation using un-doped, Tb³⁺ and Eu³⁺ doped nanocatalysts are summarized below [15, 16]

$$TiO_2 + hv \rightarrow h^+ + e^-$$
Essentially, every photocatalytic reaction is a special kind of photochemical reaction. During environmental photocatalysis, the oxidation ability of the photo-induced holes is mainly employed. The separation and recombination of photo-stimulated charge carriers experience podgy competition, and the photocatalysis becomes effective only when the carriers are trapped on the particle surfaces. Moreover, the dynamic behaviour of photo-induced charge carriers, such as, transfer, capture, separation and recombination, can affect the photocatalytic activity to a great extent. The percentage of MO degradation by different nanotitania photocatalysts are depicted in Fig. 6.4.
Fig. 6.3 UV-Vis absorption spectra of MO loaded (a) un-doped TiO$_2$ (T2), (b) Tb$^{3+}$-doped (TbT3) and (c) Eu$^{3+}$-doped TiO$_2$ (EuT3) catalysts under UV light illumination of varying time durations.

Fig. 6.4 Quantitative assessment of photocatalytic performance for different nanocatalysts
The degradation capability of each of the samples, under UV irradiation, follows an increasing trend with an increasing duration of the exposure time. The doped nanotitania specimens are found to display an augmented photocatalytic performance wrt the un-doped nanotitania catalyst. It is quite evident that, Eu$^{3+}$ doped TiO$_2$ specimen is about 10-12 times more efficient than the un-doped counterpart. The photocatalytic degradation experienced a saturation trend beyond 45 min. of the UV-exposure. As can be seen from the absorption spectra [chapter III, page no. 91], the absorption edge of the TiO$_2$ nanosystem, upon Eu-doping, gets red-shifted owing to the band gap narrowing and enabling enhanced photodegradation. The reason for the increased photodegradation efficiency is ascribed to the introduction of Eu$^{3+}$ doping states which helped inhibiting $e^-h^+$ pair recombination while enhancing interfacial charge transfer reaction. As predicted earlier, the presence of intermediate trap centers, such as, impurity states and defect states are capable of reducing the recombination time thus enhancing photocatalytic activity to a great extent [17].

In case of Tb doped sample, 2.5% Tb$^{3+}$ doped nanotitania sample had a better catalytic performance over the 5% Tb$^{3+}$ doping case. In the latter case, the response can be attributed to the lowering of thickness of the space charge layer. A space charge layer is normally expected at the semiconductor-dye interface and the thickness ($d_s$) of this layer is inversely proportional to the dopant concentration [18]. When the thickness is comparable to, or more than the penetration depth of light, the charge carriers are well separated [18]. When the dopant concentration is increased above the critical limit, $d_s$ becomes very small and under this situation, the charge carriers would undergo recombination with great ease. Consequently, only a few free electrons and holes can be available for interaction with the dye molecules. A scheme, highlighting photocatalytic degradation and the formation of free radicals is illustrated in Fig. 6.5.
The kinetics of photocatalytic decomposition of the organic compound (MO) at the nanocatalyst surfaces can be understood through Langmuir-Hinshelwood (L-H) model [19]. This mechanism proposes that molecules fairly adsorb and the adsorbed molecules undergo a bi-molecular reaction. The rate of heterogenous reaction is controlled by the reaction of the absorbed species, and that all adsorption and desorption pressure are in equilibrium. For a solid-liquid reaction, it can be expressed as:

\[
 r_i = -\frac{dC}{dt} = \frac{k\alpha C}{1 + \alpha C} \tag{6.5}
\]

where, \( r_i \) represents the initial rate of photo-oxidation, \( C \) the concentration of the reactant (here, \( C \) is the MO concentration), \( t \) the irradiation time, \( k \) the rate constant of the reaction and \( \alpha \) is the adsorption coefficient of the reactant. For a very dilute solution (mM concentration, \( C \ll 1 \)), one can safely use pseudo-first-
order kinetics and the above equation can be simplified into the following form [19],

\[ C_t = C_0 e^{-k_a t} \]  

(6.6)

or,

\[ \ln \frac{C_t}{C_0} = -k_a t \]  

(6.7)

where \( k_a \) is the pseudo-first order rate constant and can be predicted from the slope of the graph of \( \ln C/C_0 \) versus \( t \), the irradiation time and \( C_0 \) being the initial concentration of the MO solution (Fig. 6.6(a)). At \( t=0 \), \( C_t = C_0 \). The reaction constant, \( k_a \) was estimated to be 0.001, 0.004, 0.014 and 0.002 for T2, TbT1, TbT2 and TbT3 specimens; respectively. And the respective \( k_a \) was estimated to be 0.0036, 0.0042 and 0.0071 for EuT1, EuT2 and EuT3 specimens. The number of exchangeable OH groups for MO adsorption can also be calculated for TiO2 (T2), Tb3+ doped TiO2 (TbT3) and Eu3+ doped TiO2 (EuT2) nanoparticles, which turn out to be 3.2/nm², 13.3/nm² and 10.9/nm² [18]. The respective BET surface areas, as calculated from the \( N_2 \) adsorption-desorption traces, are found as 93.97 m²/g, 380.45 m²/g and 311.24 m²/g for T2, TbT3 and EuT2. Consequently, the total number of MO adsorption active sites, in 3 mM of T2, TbT3 and EuT2 samples, are of the order of \( \sim 7.5 \times 10^{19}, 1.25 \times 10^{21} \) and \( 8.5 \times 10^{20} \); respectively. In a 5 mL of solution, therefore, the number of MO dye molecules is approximately, \( 9 \times 10^{16} \). Being the number of surface adsorption sites invariably larger than the MO molecules, almost all the dye molecules are likely to be adsorbed completely. Since the change in the number of dye molecules in the reaction is negligible as compared to the variation in the dye adsorption sites, the underlying mechanism is certainly mediated by a pseudo-first order reaction [21].
Fig. 6.6 The photocatalytic degradation kinetics is assessed through pseudo-first order kinetics by plotting \( \ln \frac{C}{C_0} \) vs. exposure time, \( t \).

On comparing the photocatalytic performance of the un-doped and RE ion doped nanotitania, we found that it is the doped sample which shows the augmented photocatalytic response. Among Tb\(^{3+}\) and Eu\(^{3+}\) doped nanotitania, Eu\(^{3+}\) doped nanotitania seems to be a promising candidate for MO degradation under UV light. The degradation efficiency of the EuT3 is highest among all the three nanocatalyst. The degradation efficiency is about 85% for EuT3. In case of Tb\(^{3+}\) doped sample, TbT2 specimen characterizes photocatalytic MO degradation as higher as ~45%.

There is no direct link between the adsorption and surface area among RE ion doped titania; other than that at higher surface areas the capacity for adsorption tend to increase. Moreover, an enhanced surface area would result in better degradation of pollutant/organic dyes only if the adsorption is also enhanced. It appears that, the characteristic of the RE is vital in determining the surface area and adsorption ability of the doped nanocatalyst. While all RE can form complexes with many molecules, their ability to aid adsorption of specific pollutants may differ. If proper adsorption of pollutant is not achieved, it may
scatter light, thus giving lower photocatalytic activity regardless of what wavelengths are used [22]. Hence by selecting suitable RE ion as dopant an enhanced photocatalytic activity can be achieved.

6.3 **A comparative view on radiative emission response and photocatalysis**

A justifiable relationship between photoluminescence phenomenon and photocatalysis needs thorough, yet complicated analysis wrt various kinds of recombination processes that might occur in titanium dioxide system [16, 22-24]. It is worth mentioning here that, photoluminescence is caused by direct radiative recombination of carriers and that, the light emission intensity decreases with the lowering of recombination rate. In contrast, a higher performance of photocatalyst stems from a larger value of carrier life-time. In other words, suppressed recombination events would help improving the photocatalytic activity at large [25]. By introducing suitable dopants into the host, select emission response can be achieved via indirect radiative recombination, along with appreciable photocatalytic responses. The simultaneous photoluminescence and photocatalytic performances are highly demanding for monitoring environmental remediation and staining specific surfaces. In this regard, Tb\(^{3+}\) and Eu\(^{3+}\) doped nanotitania being an alternative candidate, can ensure not only select radiative emission but also appreciable photocatalytic activity.

6.4 **Photochromic activity of Ag\(^{+}\) doped nanotitania systems**

Photochromism is the reversible change of colour by the transient interplay of light with the solid state matter. Photochromism is derived from the Greek words, phos (light) and chroma (color). The photochromic effect is a reversible process of absorption changes in some materials induced by illumination. The
changes can be removed and the absorption can be brought into its initial state by means of light illumination. Photochromic materials are of great interest because of their immense applicability like, colour changing lenses for sunglasses and smart windows, 3D optical data storage, optical memories and switches, variable electrical current, ion transport through membranes, variable wettability, etc. [26]. Photochromic materials in nanoscale form are particularly interesting. The nanoparticles of photochromic material can be dispersed in aqueous solution forming colloidal suspensions or can be incorporated in thin-layer matrices, avoiding problems of light scattering or shallow light penetration in bulk materials, with desirable performance. Nanotitania film loaded with Ag doped TiO$_2$ nanoparticles is of great interest because of its properties like rewritable colour copy paper, smart glass, multiwavelength optical memory, holographic data storage or rewritable data carriers [27-31].

To increase functional properties, TiO$_2$ structures can be doped with metal ion. Photochroism can be visualized in Ag doped nanotitania film. The process of photochroism entails the oxidation and reduction of surface loaded silver nanoparticles. As metallic silver nanoparticles display surface plasmon resonance (SPR), intensely coloured films are observed when the nanoparticles are in their reduced state (Ag$^0$). This intense colour arises from the coupling of EM wave with electronic excitations in the metal that propagate at the boundaries. The reduced metallic state is formed through UV irradiation, where the photo-excited electrons from the underlying TiO$_2$ film reduce any silver oxide (Ag$_2$O) to silver metal (Ag). When the UV light is removed, the metallic silver particles slowly revert to their oxidized state slowly.

The photochromic materials change their colour reversibly by the action of light. The properties of photochromic materials not only depend on the nature of each
of the constituents, but also on the interface and synergy between them. Since the charge transfer plays a key role in the photochromic activity of these materials, it is very important to induce charge (electrons, holes, and protons) interactions between the two components in either composites or hybrids. Photochromic activity is due to the surface photoreduction (i.e., impurity ion is adsorbed at the surface or the interfaces) [32].

![Fig. 6.7](a) Photograph of UV irradiated sample 1, 2 (A2 and A3) and 3 (prepared via sol-gel route), (b) Trace showing $\lambda_T$ vs. $\lambda_I$ for three Ag-TiO$_2$ specimen films.

TiO$_2$ can be coloured by a band-gap excitation due to trapping of electrons as Ti$^{3+}$ species, and photochromism is rarely observed in the absence of hole scavenger species [33]. In the present case, the initial colour of the film was found to change upon 5 mins of UV light ($\sim$350 nm) illumination as observed from Fig. 6.7(a). Films 1, 2 (A2, and A3 prepared by solid state quenching for cycle 2 and 3 respectively, chapter II, page no 66) and 3 (prepared by sol-gel method chapter II, page no 59) upon 5 mins of UV light irradiation, get converted to dark cyan, dark brown and dark olive colours; respectively. After a time duration of $\sim$6 h, the films have regained their original colour. The Ag doped TiO$_2$ nanoparticles are
associated with photoexcitation and reduction of Ag$^+/Ag^*$ can be revealed with transfer of electrons from the host TiO$_2$ to Ag [34]. The original colour of the films were regained by removing excess Ag$^+$ obtained under UV light [33]. In order to substantiate further, transmission response of different films was considered while incident wavelength of light was varied within 225–900 nm. Using a well known relation, $\lambda_T = \frac{\lambda_I}{T}$, with $\lambda_I$ and $\lambda_T$ representing incident and transmitted wavelengths and $T$ being transmittance, plotted of $\lambda_T$ versus $\lambda_I$ which are presented in Fig. 6.7(b) [35]. It is clear from the trend that the transmitted light wavelength attains a maxima which correspond to an incident wavelength of 630 nm. One can find from the spectra that, in the lower wavelength side of the incident light, transmitted light experiences a smaller wavelength value thereby depicting a higher transmittance response. As we move toward a higher wavelength side of the incident light, the transmitted light wavelength increases and reaches a maxima at $\sim$630 nm of the incident light and follows a decreasing trend. Moreover, film 1 exhibits a maximum wavelength of transmitted light ($\sim$2250 nm). In contrast, films 2 and 3 corresponded to transmitted light wavelength with respective maxima at $\sim$1150 and 1300 nm. This could be related to the particle size effect of Ag-doped TiO$_2$ system. Note, the particle size of TiO$_2$ in film 1, which is larger than that in film 2 which was prepared by two LN2 quenching cycles whilst film 3 was developed using sol-gel method (chapter II, page no. 67).

### 6.5 Concluding remarks

Nanotitania is advantageous over other photocatalysts since it is not only, cheap, but also readily available, while exhibiting strong catalysing power. In summary, each RE ions could add value to TiO$_2$ in a comparable. The recombination reaction was delayed by creating oxygen vacancies and impurity levels which
acted as electron traps thus improving its photoactivity. The BET surface analysis of Tb$^{3+}$ doped nanotitania specimen has revealed a more-open hysteretic isotherm along with a steeper tailing as compared to both the un-doped and Eu$^{3+}$ doped titania systems. The catalytic activity, under UV light illumination, is discussed in the light of pseudo-first order kinetics while 5% Eu$^{3+}$ and 2.5% Tb$^{3+}$ doped nanotitania specimen displaying the maximal efficiency. An augmented photoluminescence and photocatalytic response is believed to emerge mostly at the surfaces of the nanoparticles, mediated via defects (e.g. oxygen vacancy). Materials which have simultaneous emission and catalytic responses would find immense scope in monitoring pollution control, remediation of contaminants while setting emission standards.

References


