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Materials Chemistry and Physics 85 (2004) 52–57

MATERIALS CHEMISTRY AND PHYSICS

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# Preparation and photo-catalytic activity of Fe–$TiO_2$ thin films prepared by sol–gel dip coating

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Received 9 September 2003; received in revised form 12 September 2003; accepted 2 December 2003

**Abstract**

Thin films of iron (Fe) doped titanium dioxide (Fe–$TiO_2$) were prepared on a variety of substrates by using Ti-peroxy sol–gel dip coating method. The surface structure of the film was modified by adding different concentrations of polyethylene glycol (PEG) into the $TiO_2$ sol. Most of the metal ion doped entered $TiO_2$ lattice resulting the shift in optical absorption edge towards visible side. Addition of PEG alters the surface morphology and structure of the films. The increase in concentration of PEG increases the number and size of the pores on surface of the film by decomposition of PEG when the films are subjected to heat treatment. The adsorbed hydroxyl content of such porous films is found to increase with amount of PEG added. Photo-catalytic properties of the surface modified and Fe ion doped $TiO_2$ catalyst was investigated by degradation of methyl orange in sunlight. The photo-catalytic activity of the PEG added Fe–$TiO_2$ catalyst was enhanced by 2–2.5 times than undoped $TiO_2$.

*Keywords:* Iron–titania; Thin films; Methyl orange; Photo-catalytic; Degradation; Sunlight

## 1. Introduction

Photo-oxidation by using $TiO_2$ photo-catalyst is being widely studied as a relatively new technique of pollution abatement [1–3]. $TiO_2$ is a commonly used photo-catalyst because of its stability in UV light and water. However, the need of an ultraviolet (UV) excitation source, restricts its technological utility for limited applications. For widespread applications, $TiO_2$ photo-catalyst effective in solar light or light from visible region of the solar spectrum need to be developed as future generation photo-catalytic material. $TiO_2$ absorbs only 5% energy of the solar spectrum hence numerous studies have been performed to extend the photo-response and photo-catalytic activity by modifying its surface structure, surface properties and composition [4–6]. The surface modification by doping with metal ions and organic polymers has been proven to be an efficient route to improve the photo-catalytic activity of $TiO_2$ [7–10]. Many researchers have paid attention in developing modified $TiO_2$ powder catalyst [11,12] but using the powder catalyst has the disadvantages like stirring during the reaction and separation of catalyst after each run. The preparation of thin film catalyst will overcome these problems and it will also extend the applications of catalyst towards antibacterial ceramic tiles as well as self-cleaning glasses [1]. Among the different thin film deposition techniques the sol–gel dip coating is the simplest, economical and has advantages such as $TiO_2$ is easily anchored on the substrates bearing the complicated shapes and large area substrates. The deposition of $TiO_2$ by sol–gel method has been reported by few authors [1,13–15]. The present paper deals with the preparation of Fe–$TiO_2$ thin film photo-catalyst by sol–gel dip coating process and modification of the surface structure by addition of polyethylene glycol (PEG, average molecular weight: 4000). The effect of addition of PEG on the nature of the films and photo-catalytic activity has been investigated.

## 2. Experimental

### 2.1. Preparation of $TiO_2$ precursor sol

The $TiO_2$ sol was prepared by using titanium tetraisopropoxide ($Ti(OC_3H_7)_4$, 99.5%, Aldrich), hydrogen peroxide ($H_2O_2$, 30%, Qualigen), Ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$,

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doi:10.1016/j.matchemphys.2003.12.007

Qualigen), and polyethylene glycol (average molecular weight: 4000, Qualigen), as starting materials. The method for preparation of $TiO_2$ sol is reported elsewhere [16], in this, the titanium tetraisopropoxide (1.77 g) was hydrolyzed with 100 ml of water and the resulting titanium hydroxide was washed thoroughly to remove alcohol formed in the hydrolysis. To this precipitate 20 ml of aqueous $H_2O_2$(15%) was added slowly and allowed to dissolve the precipitate completely. During dissolution 85 ml of distilled water was added to this solution to avoid immediate dense gel formation. Various amounts of 10% PEG solution was added to get PEG containing sol. Then 0.1 M iron (Fe) solution (0.1 M solution prepared by dissolving 0.404 g $Fe(NO_3)_3\cdot 9H_2O$ in 100 ml distilled water) was added into this sol to prepare the PEG and Fe containing $TiO_2$ sol. The above diluted titanium peroxide sol was allowed to stand for 4–5 h to form a viscous sol. The change in viscosity with time was monitored using Brookfield viscometer. Following this method the sols containing different concentrations of Fe such as 0, 1, 2, 4 wt.% were prepared.

### 2.2. Deposition of thin films

Before deposition of thin films, the substrates such as soda lime glass, silica rings and glass helix were first degreased, cleaned thoroughly and dried in an oven at 150 °C. These substrates were stored in desiccators and used whenever required. For deposition of thin films, the substrates (glass or silica plate) were dipped in the viscous titanium peroxide sol containing known concentration of Fe and PEG prepared by above method for 10–15 min and pulled out with slow and uniform pulling rate of approximately 1 mm $s^{-1}$. The viscous titanium peroxide sol adhered to the substrate was allowed to dry in open atmosphere at room temperature. A very thin and uniform film of titanium peroxide was formed on the substrate, which was further dried in an oven at 100 °C for 2 h. Following this method the films were deposited for various concentrations of PEG and Fe in $TiO_2$ sol. These thin films were further heated between 200 and 500 °C in an electric furnace to decompose the polyethylene glycol and obtain crystalline titania films. For deposition of thin films on substrates having complex surface such as glass/silica helix, silica/glass rashing rings, the known quantity of substrates were dipped into sol. The viscous sol turns into dense gel after a few hours, was allowed to dry for 6–8 days in open air atmosphere at room temperature. A thin film of iron–titania (Fe–$TiO_2$) was formed on these substrates, after heat treatment they were used for photo-catalytic reactions.

### 2.3. Photo-catalytic decomposition of methyl orange on Fe–$TiO_2$ films

Photo-degradation of organic compounds using Fe–$TiO_2$ as catalyst occurs when catalyst is illuminated with sunlight in presence of water containing dissolved oxygen and organic compound. The organic species are decomposed to $CO_2$ and $H_2O$ under these conditions

$$\text{Fe–TiO}_2 \xrightarrow{h\nu} \text{Fe–TiO}_2\ (e^- + h^+) \quad (1)$$

$$h^+ + OH^-_{ad} \rightarrow OH_{ad} \quad (2)$$

$$h^+ + H_2O_{ad} \rightarrow OH_{ad} + H^+ \quad (3)$$

$$e^- + O_2 \rightarrow {O_2}^- \quad (4)$$

where $h^+$ represents the hole with positive charge generated at the surface of catalyst. The methyl orange is attacked by hydroxyl radicals formed as given in the above equation and generates organic radicals or other intermediates. Finally the parent compounds and intermediates are oxidized into $CO_2$, ${SO_2}^{2-}$, ${NO_3}^-$ and $H_2O$.

The photo-catalytic activity of the catalyst was tested using an in-house fabricated quartz reactor. The reactor consists a quartz tube of dimensions 20 mm diameter × 250 mm length having arrangement for bubbling air during the reaction. The Fe–$TiO_2$ thin film photo-catalyst containing different concentrations of Fe was coated on silica rashing rings as the catalyst. The Fe–$TiO_2$ coated silica rings (20 g) were loaded into the reactor column. The solution of methyl orange (40 ml, 100 ppm) was fed into the reactor column and kept in dark place for 30 min. After 30 min the reactor was irradiated with sunlight for different time intervals. The air was bubbled throughout the experiment at the rate of 10 ml $min^{-1}$. The sample after irradiation was separated and analyzed with UV-visible spectrophotometer (Hitachi 3210). The differential absorbance at 490 nm for methyl orange (absorption peak methyl orange) was measured. The change in the concentration of methyl orange of the irradiated sample with time was monitored by UV-visible spectrometer and compared with the blank (i.e. silica rings without catalyst coating were used instead of catalyst coated silica ring) kept in sunlight at the same experimental conditions. The linear relationship between the absorbance at 490 nm ($A$) and the concentration of methyl orange ($C$) can be represented empirically by the equation

$$A = 0.0259 \times C \quad (5)$$

All the concentration profiles can be correlated by the following exponential function with good agreement

$$C = C_0 \exp(-kt) \quad (6)$$

The apparent rate constant $k$ in the above equation decreases with increasing of initial concentration of methyl orange when other parameters are kept unchanged. Therefore the photo-catalytic decolorization of methyl orange is pseudo-first-order reaction and its kinetics may also be expressed as [17]

$$\ln\left(\frac{C_0}{C}\right) = kt \quad (7)$$

According to Eq. (5), Eq. (7) can also be expressed as follows:

$$\ln\left(\frac{A_0}{A}\right) = kt \quad (8)$$

where $k$ is the apparent rate constant, $A_0$ the initial absorbance of methyl orange, $t$ the reaction time and $A$ the absorbance of aqueous methyl orange at time $t$. $k$ is determined by a linear regression method.

## 3. Characterization

The crystallinity of the Fe–$TiO_2$ films as well as dried bulk Fe–$TiO_2$ powder was determined by X-ray diffraction (XRD) using Rigaku (Rigaku, D-Max III VC, Japan) diffractometer with Cu Kα radiation. The accelerating voltage and the applied current were 35 kV and 20 mA, respectively. The surface morphology of the $TiO_2$ films were observed using scanning electron microscopy (SEM, Philips XL-20) with an accelerating voltage of 10–15 kV. The thickness of the films were measured by using Talley Step Profilometer (Labtech Instruments, L-100). Spectroscopic analysis of the $TiO_2$ films were performed using UV-visible spectrophotometer (Hitachi, U-3210) with wavelength range of 300–900 nm. The thermal property of the solid titanium peroxide was studied by TG/DTA (Mettler-Toledo, TGA/SDTA 851). The metal ion content of the films and dried bulk powder was analyzed by ICP-OES (Perkin-Elmer, P-1000) spectrometer. The hydroxyl content of the films was investigated by FTIR (Perkin-Elmer, Spectrum-2000) spectrometer.

## 4. Results and discussion

### *4.1. Effect of Fe and PEG addition on optical properties and microstructure of films*

The viscosity plays an important role in the sol–gel deposition process. It was observed that the film thickness increases with the increase in the viscosity of the $TiO_2$ precursor sol (Table 1). The film thickness can be adjusted by depositing the surface at particular viscosity range in only one coating cycle. At second coating cycle the sol does not get adhered to the surface uniformly and it tends to form droplets rather than a liquid film, results in non-uniform films after drying. To overcome this problem we have used water soluble organic polymer such as polyethylene glycol. The addition of 0.6 g polyethylene glycol or less than that to the $TiO_2$ precursor sol does not change optical properties of $TiO_2$ films but it improves the adhesion of the sol to the substrate and by using the sol containing PEG the films of required thickness can be obtained by repeating number of coating cycles (Table 2).

Table 1
Variation of film thickness with change in viscosity of sol

| Composition of sol | Time (h) | Viscosity of sol | Film thickness (nm) |
|---|---|---|---|
| $TiO_2$ | 5 | 1280 | 65 |
| | 6 | 1530 | 80 |
| | 7 | 2300 | 95 |
| | 8 | 2600 | 110 |

Table 2
Effect of PEG addition on the film thickness

| Composition of sol | Viscosity (cP) | Number of coating cycles | Thickness (nm) |
|---|---|---|---|
| $TiO_2$ sol | 1280 | 1 | 65 |
| | 1280 | 2 | 65 |
| | 1530 | 1 | 80 |
| | 1530 | 2 | 82 |
| | 2300 | 1 | 94 |
| | 2300 | 2 | 95 |
| $TiO_2$ sol containing 0.6 g PEG | 1280 | 1 | 70 |
| | 1280 | 2 | 85 |
| | 1280 | 3 | 95 |
| | 1530 | 1 | 80 |
| | 1530 | 2 | 100 |
| | 1530 | 3 | 115 |
| | 2300 | 1 | 100 |
| | 2300 | 2 | 130 |
| | 2300 | 3 | 155 |

Fig. 1 shows the UV-visible spectra of the films deposited by using various concentrations of PEG. The spectra shows that increase in concentration of PEG into sol decreases the transmittance of the films in 350–800 nm UV range, it may be due to the scattering of light by pores. This indicates that the difference in transmittance is related to the difference in size and number of pores. To shift the absorption edge towards visible region, the iron (Fe) was doped into the $TiO_2$ at very low level (1–4%). The addition of Fe ions into the sol changes the gel formation behavior of the sol. At pH 4 within few hours the $TiO_2$ precursor sol normally turns into gel but addition of Fe at dopant level prohibits the gel formation and it turns into sol containing gelatinous precipitate rather

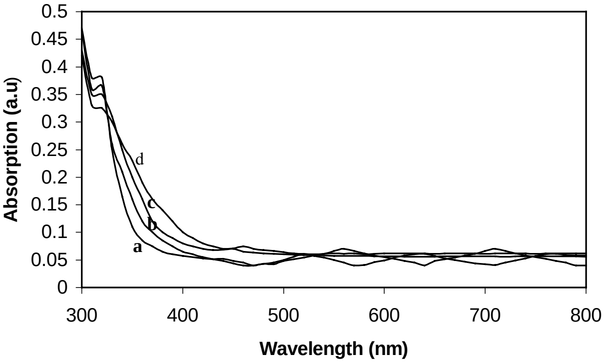

Fig. 1. UV-visible absorption spectra of the (a) 0.3 g PEG $TiO_2$, (b) 0.6 g PEG $TiO_2$, (c) 0.9 g PEG $TiO_2$ and (d) 1.2 g PEG $TiO_2$ films prepared by two coating cycles.

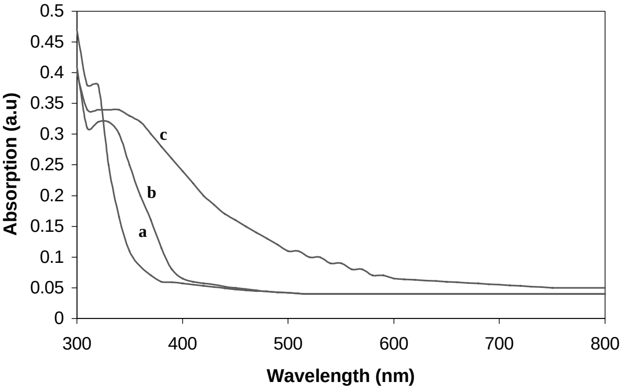

Fig. 2. UV-visible absorption spectra of (a) 0.6 g PEG $TiO_2$, (b) 0.6 g PEG 2% Fe–$TiO_2$ and (c) 0.6 g PEG 4% Fe–$TiO_2$ films prepared by two coating cycles.

than a gel. The gelly precipitate after few hours separates into two layers, the upper layer is the solvent and the other is gelatinous precipitate. This may be because the Fe ion restricts gel network to smaller networks. The addition of PEG into the sol not only improves the gel behavior but also helps in formation of porous films. Fig. 2 shows the UV-visible spectra of the films deposited by using sol containing PEG (0.6 g) and different concentrations of Fe (0–4%). In these spectra it can be seen that, the absorption of pure $TiO_2$ films is at around 340 nm and addition of PEG does not shifts the absorption edge. However the films deposited by using $TiO_2$ sol containing various concentration of Fe shows the shift of absorption toward visible spectrum. The increase in concentration of dopant shows not only shifts the absorption edge towards the visible but also increases the absorption of $TiO_2$ in whole visible range (400–800 nm). The thickness of the Ti(IV) oxide films on glass, silica plates was measured by Talley Step Profilometer. For this measurements, the half surface of the plate was coated on one side and the height of the step, i.e. difference between the uncoated surface and coated surface was measured.

The effect of PEG addition on surface microstructure of the films was investigated by scanning electron microscope (SEM). Fig. 3a–c shows the SEM images of the Fe–$TiO_2$, 0.3 g added 2% Fe–$TiO_2$ and 0.6 g PEG added 2% Fe–$TiO_2$ films, respectively. It is observed that, 2% Fe–$TiO_2$ film prepared without addition of PEG (Fig. 3a) is non-uniform in thickness and having cracks at many places whereas the film prepared by addition 0.3 g PEG into the sol is uniform with granular texture and without cracks. However the film prepared by addition of 0.6 g PEG into the sol has pores at the surface after decomposition of PEG at 450 °C. It is therefore concluded that the films prepared by addition of PEG are porous in nature.

The effect of PEG addition on hydroxyl content of the films was investigated, by addition of various concentrations of PEG into Fe–$TiO_2$ sol and films were deposited by using these sols on soda lime glass (Fig. 4). The soda lime glass

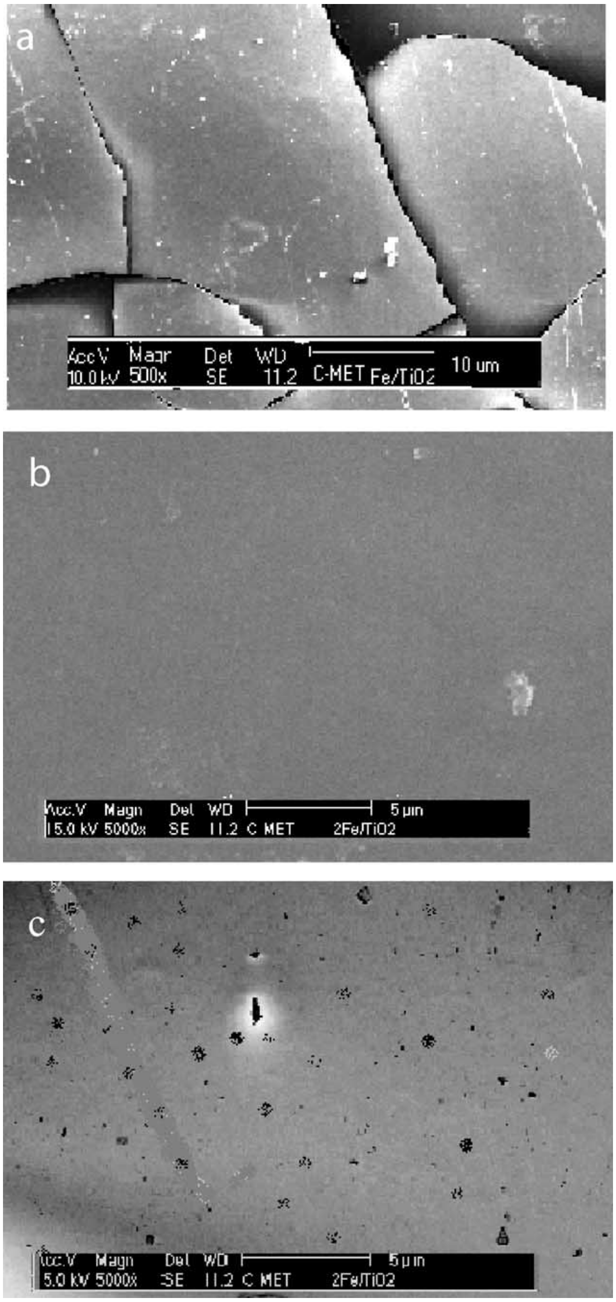

Fig. 3. SEM images of the thin films prepared on soda lime glass: (a) 2% Fe/$TiO_2$, (b) 0.3 g PEG 2% Fe–$TiO_2$, (c) 0.6 g PEG 2% Fe–$TiO_2$.

shows complete absorption in the region of 400–2000 $cm^{-1}$ hence the spectra were recorded in 2000–4000 $cm^{-1}$ region only. The spectra of the films deposited by using 2% Fe–$TiO_2$ containing various concentrations such as 0, 0.3, 0.6 and 1.2 g PEG (curves a–d) shows the increase in intensity of peak at around 3500 $cm^{-1}$ corresponding to the various hydroxyl groups (attached or adsorbed OH to Fe–$TiO_2$) with increase in added PEG content. This suggests that the hydroxyl content of the films increases with respect to the increase in added PEG into the sol used for deposition of films.

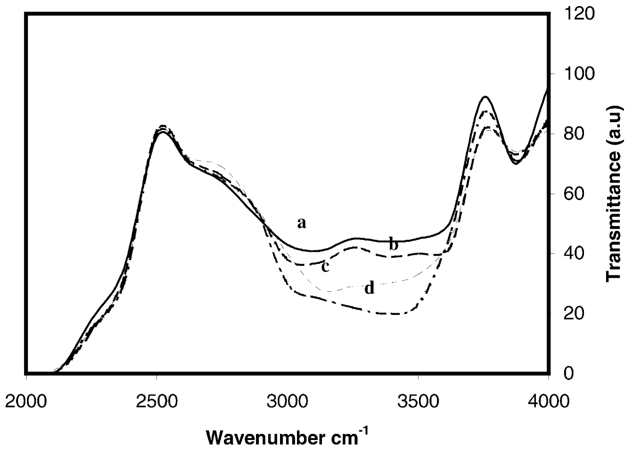

Fig. 4. FTIR spectra of films of (a) Fe–$TiO_2$, (b) 0.3 g PEG Fe–$TiO_2$, (c) 0.6 g PEG Fe–$TiO_2$ and (d) 1.2 g PEG Fe–$TiO_2$ on soda lime glass.

### 4.2. Crystallization of films and gel

The TG/DTA curve for the sample of pure gel is shown in Fig. 5. The TG curve show weight loss in two stages with an endothermic peak at 150 °C and exothermic peak at 250 °C. The total weight loss of around 34% is observed between 40 and 250 °C in two stages. The weight loss is attributed to the loss of absorbed water in the titanium peroxide gel and the conversion of peroxide to oxide, respectively. There is no further loss in weight but an exothermic peak can be seen at around 500 °C which is due to transformation of anatase phase of $TiO_2$ to rutile [16]. The beginning of such transformation at around 500 °C is also indicated in the XRD pattern of the sample.

The films deposited as well as the dried gel powder was heat treated at different temperatures and XRD pattern were recorded (Fig. 6). The XRD pattern of sample dried at 100 °C shows very weak peaks corresponding to anatase phase indicating that the Fe–$TiO_2$ films as well as dried gel was amorphous in nature. Upon heat treatment at temperatures from 200 to 500 °C for 3 h, a diffraction peak corresponding to the (1 0 1) plane of anatase phase appeared on the pattern. The crystalline phase of all heat treated samples (except the sample treated at 500 °C) was predominantly anatase. The sample treated at 500 °C shows some weak peaks characteristic of rutile phase. This shows that the anatase phase is stable below 500 °C and after that rutile phase starts to grow.

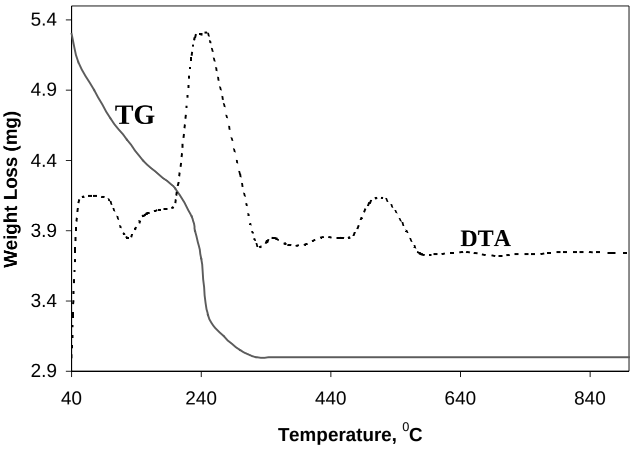

Fig. 5. TG/DTA curve of 2% Fe–$TiO_2$ catalyst powder dried at room temperature.

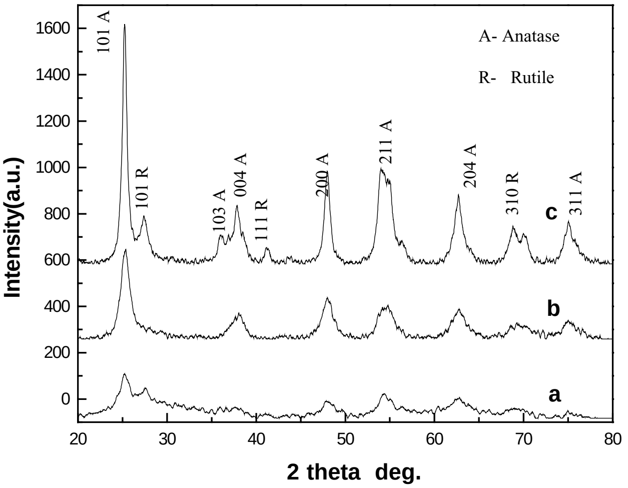

Fig. 6. XRD pattern of samples containing 0.6 g PEG, 2% Fe–$TiO_2$: (a) as prepared and dried at 100 °C for 2 h, (b) calcined at 250 °C for 2 h, (c) calcined at 500 °C for 2 h in air.

### 4.3. Estimation of Fe content of the photo-catalyst

The iron (Fe) content of the thin film catalyst was analyzed by using inductively coupled plasma optical emission spectrometer (ICP-OES) technique. For this the gel after drying was used. In this estimation, known weight of dried bulk powders containing various amounts of Fe were dissolved in the mixture of $H_2SO_4$:$H_2O_2$ (3:1). After complete dissolution of powder catalyst the solution was diluted to known volume and used as a solution for estimation of Fe content. The results are presented in Table 3.

### 4.4. Photo-catalytic activity

The plot of change in concentration of methyl orange with time of irradiation (Fig. 7) shows that, by using sil-

Table 3
Results obtained by analysis of photo-catalyst powders by ICP-OES

| Catalyst | Iron added in the sol (%) | Iron estimated by ICP-OES |
|---|---|---|
| 2% Fe/$TiO_2$ | 2 | 1.93 |
| 4% Fe/$TiO_2$ | 4 | 3.90 |
| 0.6 g PEG, 2% Fe/$TiO_2$ | 2 | 1.89 |
| 0.6 g PEG, 4% Fe/$TiO_2$ | 4 | 3.95 |

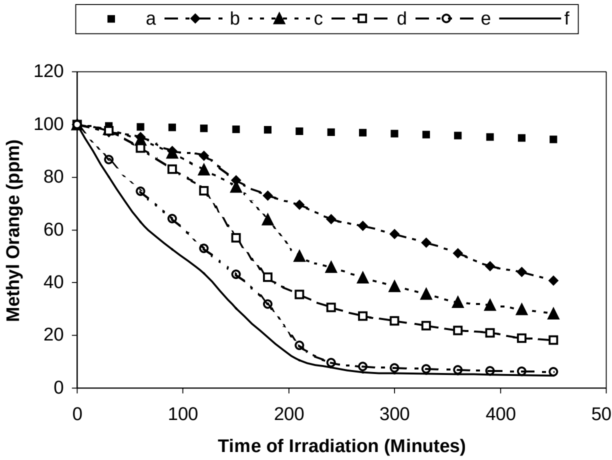

Fig. 7. Rate of decomposition of methyl orange in sunlight by using (a) blank, (b) $TiO_2$, (c) 2% Fe–$TiO_2$, (d) 4% Fe–$TiO_2$, (e) 0.6 g 2% Fe–$TiO_2$ and (f) 0.6 g 4% Fe–$TiO_2$ thin film photo-catalyst.

ica rashing rings without catalyst coating (blank sample) only 5% methyl orange was decomposed in 7 h but within same time interval the $TiO_2$ coated catalyst decomposes 50% methyl orange. Using 2% Fe–$TiO_2$ and 4% Fe–$TiO_2$ the photo-catalytic activity was increased and 50% methyl orange was decomposed within 4 and 5 h time, respectively. The addition of 0.6 g PEG in 2% Fe–$TiO_2$ and 4% Fe–$TiO_2$ increased the photo-catalytic activity of the catalyst further and 95% of the methyl orange was decomposed in 3.5 and 3 h, respectively.

The increase in photo-catalytic activity with Fe doping is related to shift in optical absorption of the catalyst in visible region. $TiO_2$ absorbs only UV energy (below 400 nm) whereas Fe doped catalyst absorbs UV and portion of visible energy hence there is increase in photo-catalytic activity. The addition of PEG into the Fe–$TiO_2$ alters the surface structure of the films, i.e. the films are porous and number and size of pores is dependent on amount of PEG addition. The more number of pores increases the hydroxyl content of the films. In heterogeneous photo-catalysis, the illumination of semiconductor produces electrons ($e^-$) and holes ($h^+$). The holes ($h^+$) are combining with $OH^-$ ions and there is formation of hydroxyl radicals ($h^+ + OH^- \rightarrow {}^\bullet OH$). These surface hydroxyl radical formed on the surface of the photo-catalyst are oxidizing species which ultimately affects the photo-catalytic activity (16). This suggests that the increase in hydroxyl content of the film increases the photo-catalytic activity.

## 5. Conclusions

A very simple method for the deposition of thin films of Fe–$TiO_2$ on various substrates like glass plates, silica rashing rings and glass helix has been developed. The surface hydroxyl content of these films improves the photo-catalytic activity of the photo-catalyst. The addition of Fe into the sol lowers the crystallization temperature as well as phase transition temperature. The films prepared with 0.6 g PEG containing 2% Fe–$TiO_2$ and 4% Fe–$TiO_2$ shows excellent photo-catalytic activity after heat treatment at 450 °C, up to 95% of methyl orange can be decomposed in sunlight within 3–4 h by using these catalysts.

## Acknowledgements

The authors are thankful to the Head, Catalysis Division and the Director, National Chemical Laboratory, Pune for support. RSS is thankful to the Director, Centre for Materials for Electronics Technology, Pune for encouragement, Mr. S.K. Apte for FTIR analysis and Dr. Tanay Seth for SEM analysis.

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