

Preparation of titanium(IV) oxide thin film photocatalyst by sol–gel dip coating

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Abstract

Thin films of titanium dioxide (TiO₂) were deposited on variety of substrates by a simple sol–gel dip coating technique. The substrates were coated with titanium peroxide precursor solution of controlled viscosity at a constant pulling rate of 1 mm s⁻¹, air-dried and further heated at 400 °C to obtain uniform films with good adhesion to the substrate. The change in viscosity of the peroxide solution with time and the variation of film thickness with viscosity of the gel were studied to optimize the deposition parameters. Films of titanium oxide as well as the dried powder of bulk gel were characterized by different techniques like X-ray diffraction (XRD), UV–Vis, scanning electron microscopy (SEM), N₂ adsorption and thermogravimetric differential thermal analysis (TG-DTA) techniques. The titanium oxide films deposited by this technique were 20–100 nm thick with a particle size of 4–10 nm and showed anatase structure. The titanium oxide films were found to be very active for photocatalytic decomposition of salicylic acid and methylene blue.

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1. Introduction

Growing social concern about the impact of different chemicals on the environment has focussed attention on finding ways for more effective pollution abatement methods. Following this, one of the more promising techniques is to use a photocatalytic route to oxidize such chemicals. Research on photocatalytic reactions mediated by semi-conducting oxides received considerable boost after the work of Fujishima and Honda [1]. Since then, much work on the TiO₂-mediated heterogeneous photocatalysis has been reported. So far no other substance superior to TiO₂ has been found as a photocatalyst. TiO₂ is superior than other substances because of its high photocatalytic activity and chemical stability in aqueous solution under UV light irradiation.

Recently, large number of studies appeared based on the photocatalytic activity of TiO₂ for oxidation of organic chemicals, obviously the most potential environment-friendly process [2–4]. In general, two methods of application of TiO₂ in photocatalysis have emerged, one as highly dispersed fine particles on porous support materials and suspended fluids in liquid medium [5–7] and

another as their films [8–13]. When the suspension TiO₂ is used for photodegradation of organic compounds, the suspended TiO₂ must be separated after each reaction. This problem could be avoided by using the TiO₂ films on different substrates. TiO₂ thin films are prepared by coating the substrate with a TiO₂ sol by different techniques such as chemical vapor deposition [14], chemical spray pyrolysis [15], electrodeposition [16,17], and sol–gel method [18]. Each method has its own advantages and disadvantages.

The films obtained by these techniques are porous in nature. The fine particles that make up the film have several advantages such as large specific surface area, short diffusion distance, and quantum size effect as the particles are <10 nm in diameter.

In the present work, we have developed a very simple, efficient and cost-effective method for deposition of thin films of anatase TiO₂ on various substrates by using the titanium peroxide (titanium peroxo complex) as Ti-precursor. The advantages of the sol–gel method are: it is very simple and easy for operation, films are easily anchored on the substrate and it can be used for the deposition of substrates which has complex surface or large surface area. The method is also suitable for deposition on other substrates like stainless steel plates, alumina plates, silica/glass rashig rings, silica/glass helix and glass wool.

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2. Experimental

2.1. Preparation of TiO_2 precursor sol

In the preparation of Ti-precursor sol, titanium(IV) tetrabutoxide (4.8 g, Aldrich chemicals) was hydrolyzed with deionized water (100 ml), the resulting titanium hydroxide precipitate was separated by decantation and washed thoroughly with water until the alcohol generated during hydrolysis of titanium alkoxide was completely removed. The precipitate was dissolved in 75 ml of aqueous hydrogen peroxide (30% Qualigen-make) to get a transparent orange sol of titanium peroxy complex. The sol was diluted with water to obtain the solution of different concentrations, after dilution the color of the sol changes from orange to yellow. The detailed process is shown in the flow chart (Fig. 1).

2.2. Preparation of thin films of TiO_2

For the deposition of film, the substrates were first degreased, cleaned thoroughly and dried before deposition. Then the substrate was dipped in the viscous Ti-precursor sol of known viscosity and pulled out with a uniform pulling rate of 1 mm s^{-1} , and then dried at room temperature. Following this method, films were deposited with precursor sol of different viscosities to study the relation between the viscosity of precursor sol and film thickness. A very thin film of TiO_2 formed on the substrate was first dried in air at room temperature followed by drying at 100°C for 2 h in an electric oven. The films formed were further heated at 400°C for 1 h in an electric furnace in air. By using this method the films on the substrates like glass plates, stainless steel plates and quartz plates were deposited, but for the deposition on the substrates like glass helix and silica rashig rings, the substrates were dipped into the viscous sol and the sol was allowed to dry for 6–8 days. A thin film of titanium peroxy complex was formed on the substrate and after heat treatment they were used for photocatalytic reaction. Even though we have prepared films on other substrates like stainless steel, aluminum and ceramic plates, the films deposited on glass substrates were studied in detail for structural and photocatalytic behavior for sake of convenience.

2.3. Photocatalytic decomposition of salicylic acid and methylene blue on TiO_2 films

The photocatalytic activity of the catalyst was tested using a Rayonet photochemical reactor (Rayonet, Type R-5, photochemical reactor manufactured by the SO New England Ultraviolet). The glass helix coated with TiO_2 film was used as the catalyst. Hundred milliliters of the salicylic acid (10^{-5} M) and methylene blue solution ($2.6 \times 10^{-5} \text{ M}$) were separately taken in a Pyrex glass tube of 3 cm diameter. To this 100 cm^3 of glass helix coated with a thin film of titanium dioxide were added and the tube was irradiated with a 150 W (Xe arc) UV lamp for different time intervals. The

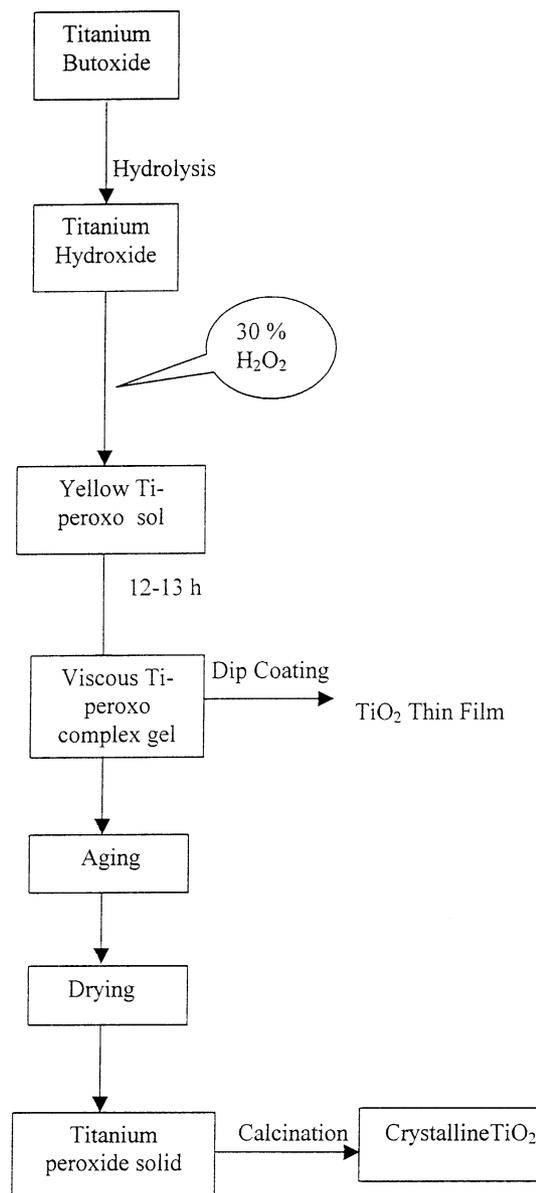


Fig. 1. Schematic diagram for preparation of TiO_2 thin film photocatalyst.

sample after irradiation was separated and analyzed with UV–Vis spectrophotometer Hitachi 3210. The differential absorbance at 296 and 662.5 nm for salicylic acid and methylene blue (absorption peaks of salicylic acid and methylene blue, respectively) were measured, respectively. The change in the concentration of the salicylic acid and methylene blue of the irradiated sample as a function of time was compared with a sample kept in darkness.

2.4. Characterization

The crystallinity of the TiO_2 films as well as the dried bulk TiO_2 powder was determined by X-ray diffraction (XRD) using Rigaku diffractometer with $\text{Cu K}\alpha$ radiation. The accelerating voltage and the applied current were 35 kV and

20 mA, respectively. The surface morphology of the TiO₂ films were observed using scanning electron microscopy (SEM, Philips XL-20) with an accelerating voltage of 20 kV. The thickness of the films were measured by using the Talley Step Profilometer. Spectroscopic analysis of the TiO₂ films were performed using UV–Vis spectrophotometer (Hitachi, U-3210) with wavelength range of 200–900 nm. The thermal property of the solid titanium peroxide was studied by TG/DTA (Mettler-Toledo, TGA/SDTA 851). The solid was heated at various temperatures and these samples were characterized by XRD (Rigaku, D-Max III VC Japan), and surface area (NOVA 1200, Quntachrome).

3. Results and discussion

3.1. Variation of viscosity of the sol with time

The change in the viscosity of the precursor sol with time was studied at room temperature by using the Brookfield viscometer having RV type of spindles. The Ti-precursor sol prepared was diluted with water to different concentrations of Ti and the change in viscosity of the precursor sol with time was studied. It was observed that the change in viscosity of the sol was concentration-dependent (as shown in Fig. 2). The viscosity initially was very low, i.e. 4–5 cps, and attains highest value within 12–36 h depending upon the concentration of the titanium ion in the sol.

3.2. Variation of film thickness with viscosity

The viscosity plays a vital role in the deposition process. The thickness of the films deposited at various viscosities was measured by the Talley Step Profilometer. It was observed that the film thickness increases with increase in the viscosity of the precursor sol (as shown in Fig. 3) up to certain limit, i.e. in between 4000 and 12,000 cps. The films deposited using Ti-precursor sol of viscosity less than

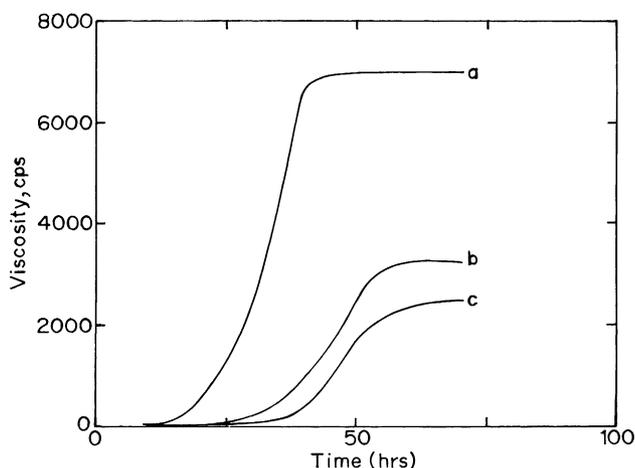


Fig. 2. Variation in viscosity with time of titanium peroxide sol having titanium ion concentration: (a) 0.01, (b) 0.005 and (c) 0.001 M.

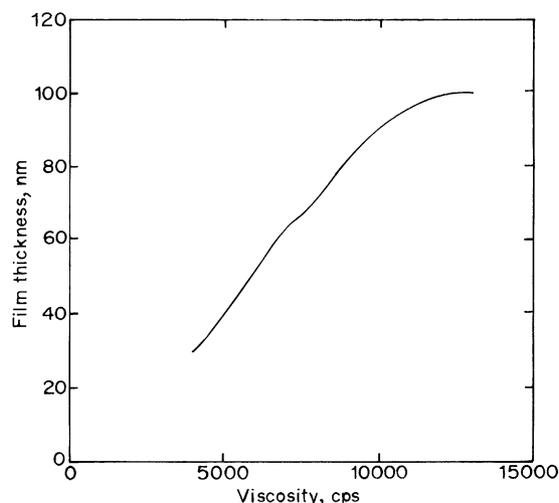


Fig. 3. Variation of film thickness with viscosity of sol.

4000 cps were having different colors at different spots which indicates that the film deposited was very thin and nonuniform. The films deposited above 12,000 cps were thick and nonuniform, but when dried at 100 °C the coated titania gets detached or it could be peeled off from the substrate. This indicates that the adhesion of the film is very poor for the films deposited above 12,000 cps compared to those deposited at lower viscosities.

3.3. Characterization of films

The thickness of the Ti(IV) oxide films on glass, silica and stainless steel plates was measured by the Talley Step profilometer. For these measurements, the half surface of the plate was coated on one side and the height of the step, i.e. the difference in height between the uncoated surface and the coated surface, was measured. The films of maximum thickness up to 100 nm can be deposited by this method.

The UV–Vis spectra of the films deposited on soda lime glass at different viscosities were recorded (Fig. 4). From the spectra, it is observed that the films are transparent in visible region and shows characteristic absorption in UV region at a wavelength of around 305 nm. The width of the absorption band increases with the increase in film thickness. The particle size of TiO₂ was calculated from UV absorption spectra of the films deposited on silica substrate by a reported method [19]. There is a shift in UV absorption edge towards the lower wavelength (blue shift) which indicates that particles which make up the film are very fine in size of about a few nanometers. The following equation was used to calculate the particle size:

$$\Delta E_{BG} = \frac{h^2}{8R_p^2\mu} - \frac{1.8e^2}{4\pi\epsilon_0\epsilon R_p}$$

where ΔE_{BG} is the difference in band gap energy, h the Plank's constant, R_p the particle radius, μ the reduced mass of the particle, e the charge and ϵ_0 is the permittivity of free

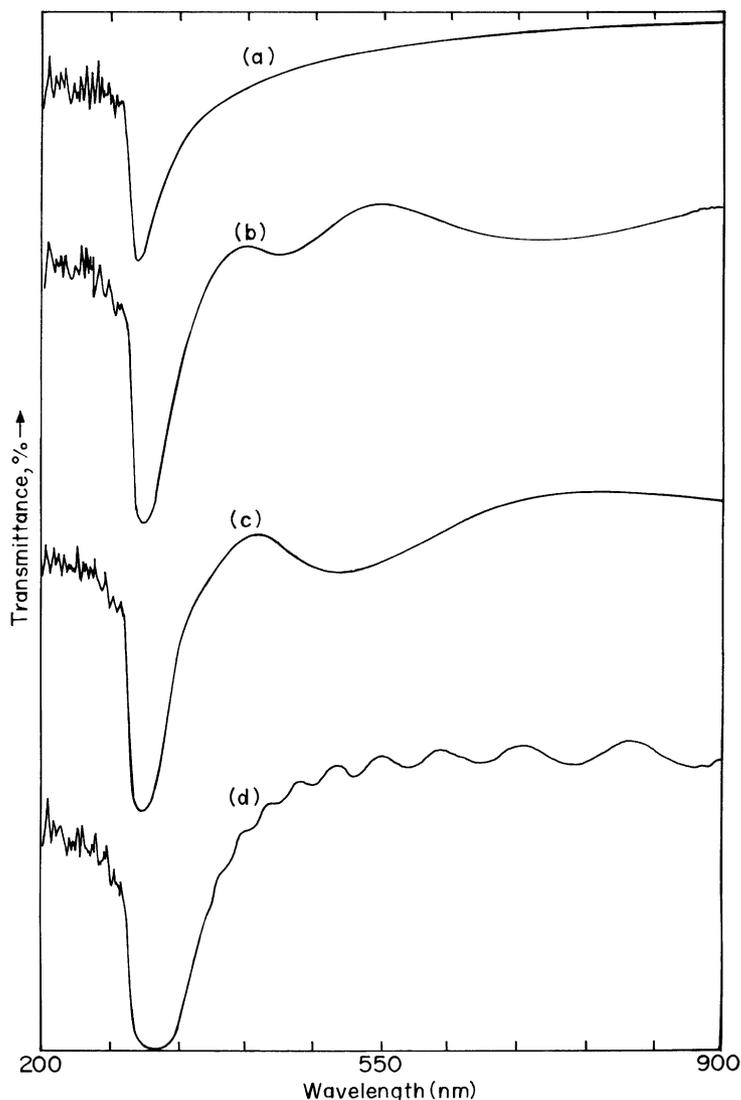


Fig. 4. UV-Vis spectra of thin films of titanium peroxide film on glass plates prepared at a uniform pulling rate of 1 mm s^{-1} by dip coating in the sol-gel aged at: (a) 8, (b) 12, (c) 18 and (d) 24 h.

space. The particle size of TiO_2 in the thin film catalyst, calculated by this equation, was in the range of 4–10 nm depending on the concentration of Ti in the precursor sol as well as aging time.

3.4. Crystal structure and morphology

The films deposited as well as the dried gel powder were heat treated at different temperatures and the XRD patterns were recorded (Fig. 5). The XRD patterns of as-prepared samples does not show any peak and indicates that the TiO_2 films as well as the dried gel were amorphous in nature. The crystalline phase of all heat treated samples (from 200 to 600°C) was predominantly anatase, whereas the sample treated at 600°C shows some weak peaks characteristic of rutile phase. This shows that the anatase phase is stable up to 500°C and after that the rutile phase starts to grow.

The SEM image reveals that the films deposited at different viscosities and the product obtained by drying the gel showed a continuous film structure (Fig. 6) and it is very difficult to find out the particle size and morphology of the sample from this image.

3.5. Thermal behavior

The TG/DTA curve for the sample is shown in Fig. 7. The TG curve shows two stages of weight loss with endothermic peak minima at 130 and 255°C , respectively. These two stages of weight loss are attributed to the loss of absorbed water in the titanium peroxide gel and the conversion of peroxide to oxide, respectively. There is no further weight loss but a broad exothermic peak can be seen in the range 600 – 1000°C with a maximum at 900°C . It may be due to the slow conversion of anatase form of

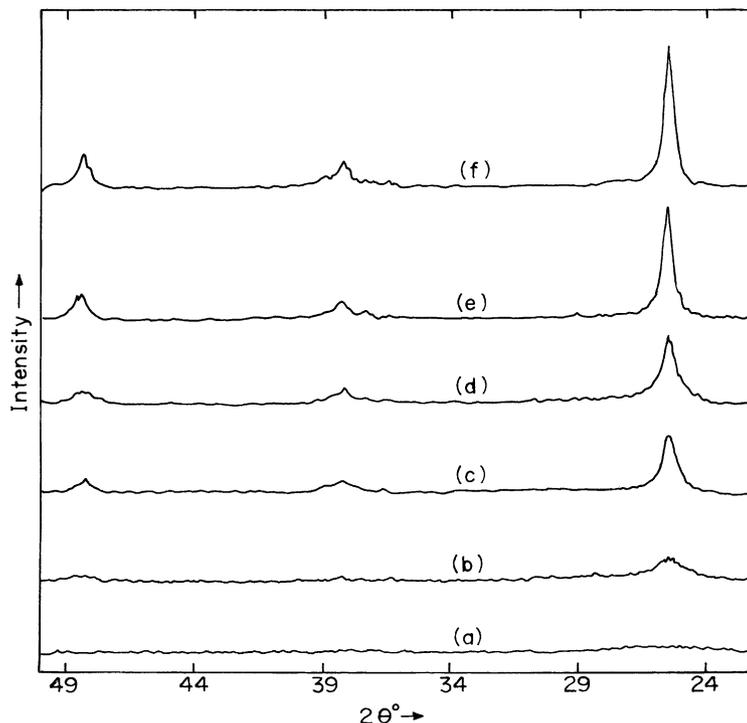


Fig. 5. XRD patterns of titanium peroxide gel heated at: (a) 100, (b) 200, (c) 300, (d) 400, (e) 500 and (f) 600 °C.

TiO₂ to rutile form. The beginning of such a transformation at around 600 °C is also indicated in the XRD pattern of the sample. The surface area of titanium peroxide sample heated at 400 °C in vacuum for 4 h was 107 m² g⁻¹ which is higher than the usually reported value for such oxide samples.

3.6. Photocatalytic activity

The activity of the thin film catalyst was determined by photo-oxidation of salicylic acid, and methylene blue. In

Fig. 8, the UV spectra of the blank salicylic acid in water (10⁻⁵ M) and reaction product of salicylic acid irradiated by UV radiation for 1 and 2 h are presented. The salicylic acid shows characteristic absorption bands at 296 nm and the intensity of this band goes on decreasing as the time of photocatalysis increases. This shows that the thin films deposited on glass helix catalyzes the decomposition of salicylic acid on exposure to UV radiation. In Fig. 9, the UV spectra of starting and product solutions of methylene blue after irradiation for 2 and 4 h are presented. The figure shows the disappearance of the band at 662.5 nm indicating that most

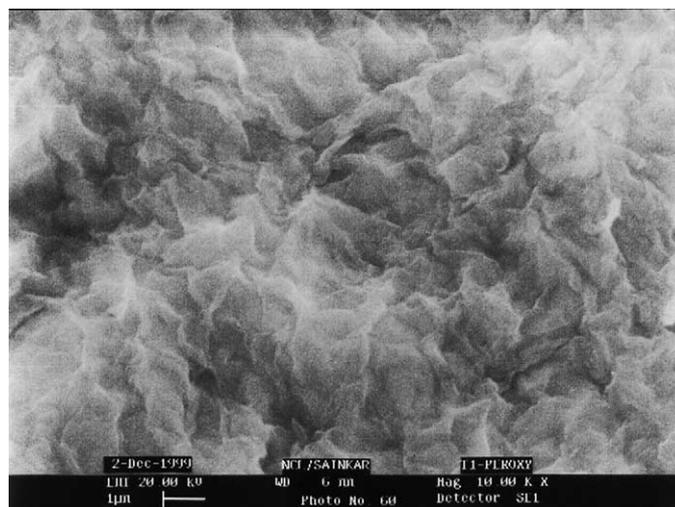


Fig. 6. SEM photograph of TiO₂ film glass dried in air at 100 °C.

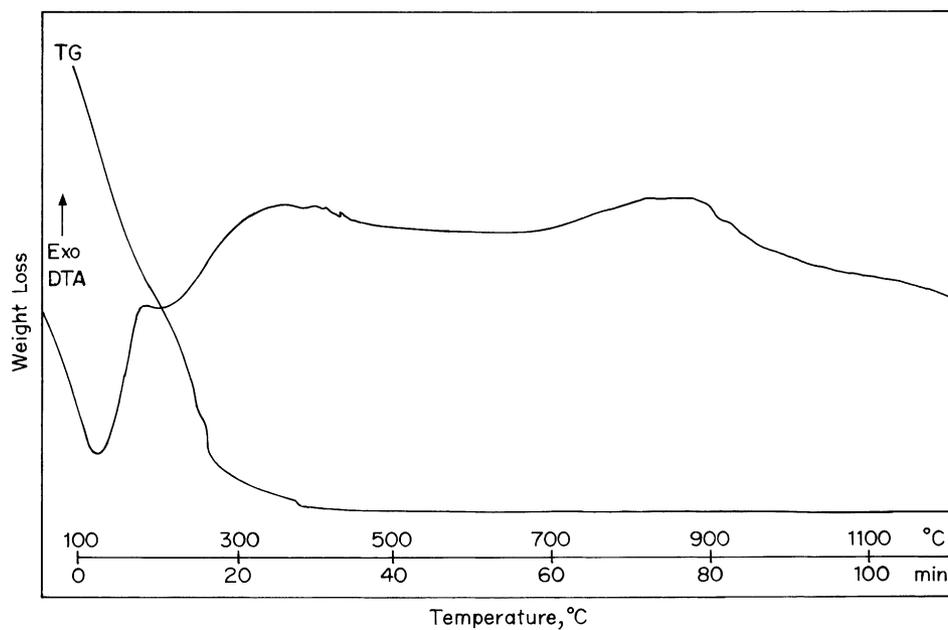


Fig. 7. TG/DTA curves of titanium peroxide gel dried at 100 °C.

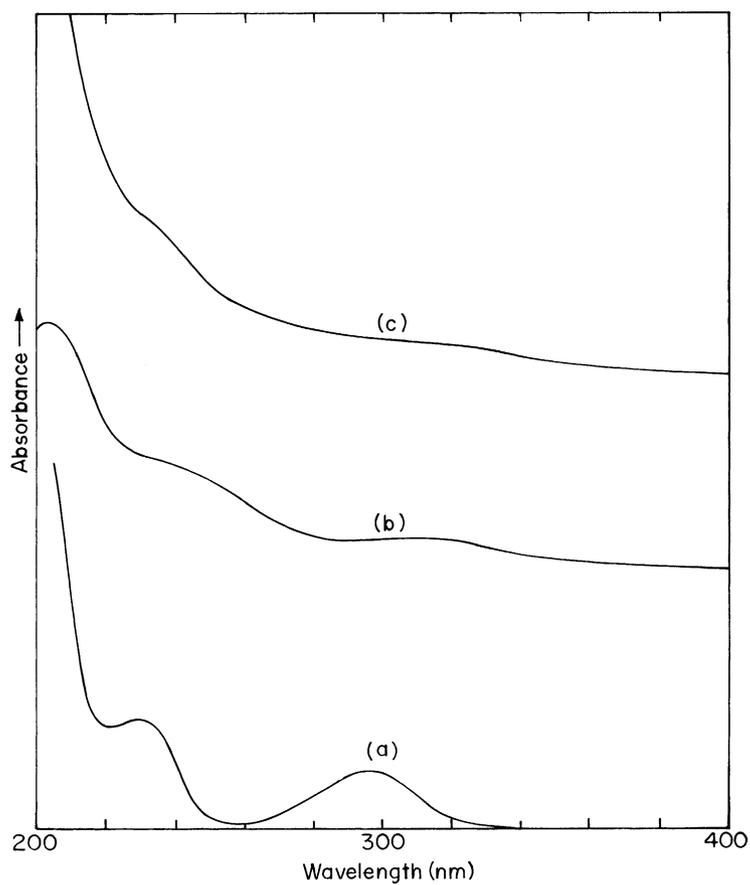


Fig. 8. UV-Vis spectra of reaction product of salicylic acid solution photocatalyzed by a thin film of TiO_2 on glass helix after UV irradiation of sample for: (a) 0, (b) 1 and (c) 2 h.

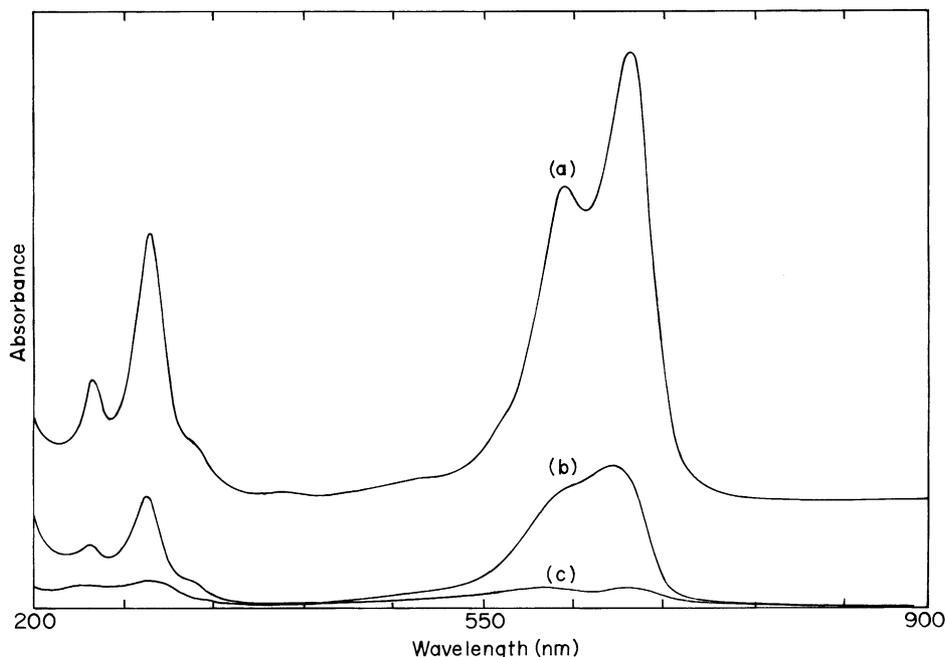


Fig. 9. UV-Vis spectra of reaction product of methylene blue solution photocatalyzed by a thin film of TiO_2 on glass helix after UV irradiation of sample for: (a) 0, (b) 2 and (c) 4 h.

of the methylene blue has been photo-oxidized within 4 h time of irradiation.

4. Conclusions

A very simple method for the deposition of thin films of TiO_2 on various substrates like glass plates, silica plates, stainless steel plates and glass helix has been developed. The films are transparent, homogeneous and uniform, and showed excellent adhesion to all the substrates. The film thickness is dependent on the concentration of titanium in the sol and the viscosity of the sol. It was found that the films deposited in the viscosity range from 4000 to 12000 cps are uniform, and adhesion is also better than the viscosity below and above this range. The films heated at various temperatures (from 200 to 600 °C) are mostly of pure anatase type. The films heated at 400 °C show excellent photocatalytic activity for the complete decomposition of salicylic acid as well as methylene blue in water.

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