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Preparation and characterization of thin film of photo-catalyst titanium oxide by dip coating method

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ABSTRACT

In this paper, a sol-gel technique with dip coating method is used to prepare photocatalytic TiO_2 thin films immobilized on glass substrate. 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 $^{\circ}C$ to obtain uniform films with good adhesion to the substrate. 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. 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), N_2 adsorption and thermogravimetric differential thermal analysis (TG-DTA) techniques. The titanium oxide films were found to be very active for photocatalytic decomposition of methyl orange and methylene blue.The photoactivity of the prepared TiO_2 thin films exhibits a comparable efficiency with TiO_2 powder,Degussa P-25.

Keywords: Semiconductors; TiO_2 films; sol-gel; methylene blue; photo catalyst.

INTRODUCTION

The sol-gel process is well known as a chemical synthesis method for the preparation of glasses. Starting from inorganic precursors such as alkoxides,soluble oxides ,or hydroxides,a growth process is initiated leading to colloids which then form three –dimensional networks by chemical aggregation. The shaping ability of sols depends on the structure and interaction between the colloidal units.It is difficult to obtain films thicker than 1µm by a one step dip-coating and densification step.

A number of methods have been employed to fabricate TiO_2 films, including sputtering, chemical vapor deposition, and sol-gel process [2,3,4]. The interest in application of sol-gel method is due to several advantages including ; good homogeneity ,ease of composition control, low processing temperature, large area coating , low equipment cost, and good photocatalytic properties[5].

The solgel methed has the method has the advantage of easy control of chemical composition of thin layers [6]. TiO_2 layers prepared by this method have been used for production of architectural windows [7, 8], as working electrodes in electro chromic devices (ECD) [9-16] and also for solar cell applications [17-24].In the last decade, TiO_2 layers have been applied in nano cell. Photo voltaic systems as a photo catalyst to remove organic pollutants from air and water and also, gas sensors, ultra filtration membranes and semi conductor devices can be based on sol-gel titania coatings [25-28].

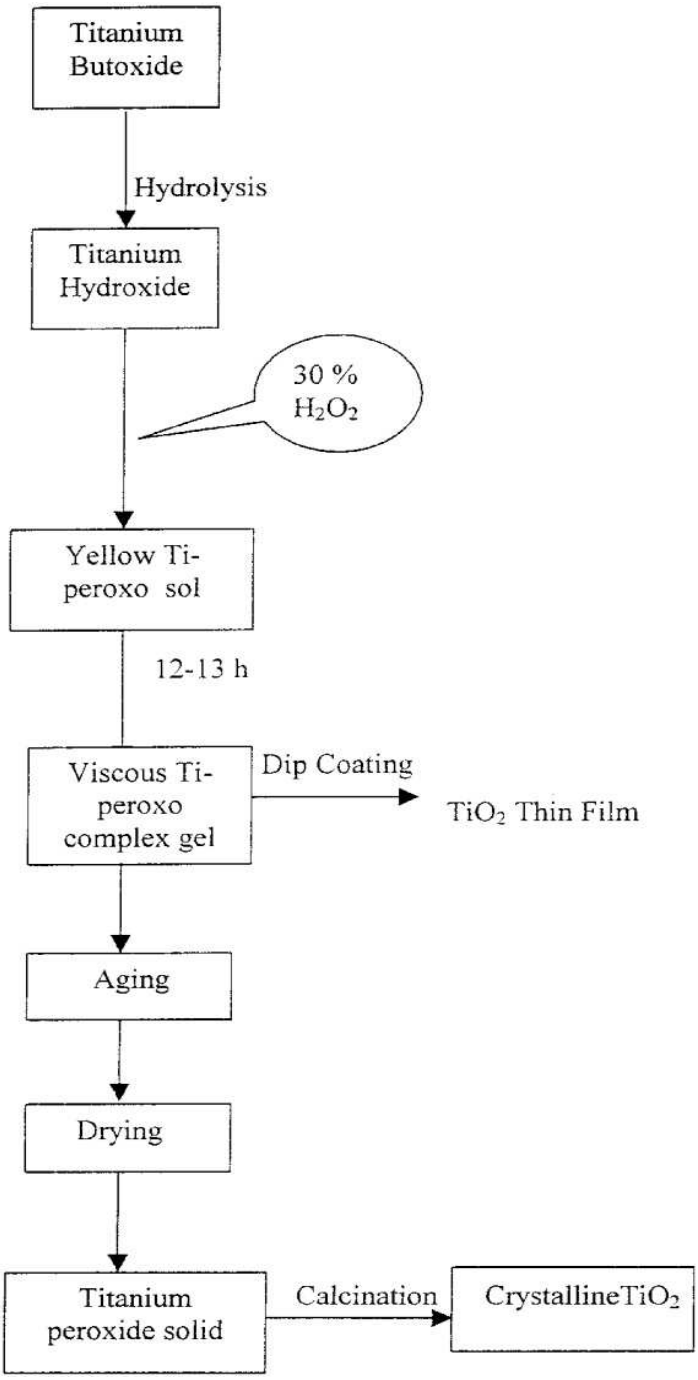

Fig. 1. Schematic diagram for preparation of TiO_2 thin film photocatalyst.

MATERIALS AND METHODS

Preparation of TiO_2 precursor sol

In the preparation of Ti-precursor sol, titanium(IV) tetra-butoxide (4.8 g, Aldrich chemicals) was hydrolyzed with deionized water (100 ml), the resulting titanium hydrox-ide precipitate was separated by decantation and washed thoroughly with water until the alcohol generated during hydrolysis of titanium alkoxide was completely removed. To get a transparent orange sol of titanium peroxo complex, the precipitate was dissolved in 75 ml of aqueous hydrogen peroxide [29].

Preparation of thin films of TIO_2

To make a film, substrates were first de-greased, cleaned thoroughly and dried before deposition. Then the substrate was dipped in the viscous Ti-precursor sol of known viscosity and pulled out , 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 $^{\circ}$C for 2 h in an elec-tric oven. The films formed were further heated at 400 $^{\circ}$C for 1 h in an electric furnace in air. By using this method the films on the substrates like glass plates, ceramics and quartz plates were deposited, but for the deposition on the substrates like glass helix and silica 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 peroxo complex was formed on the substrate and after heat treatment they were used for photocatalytic reaction [30].

Characterization

The crystallinity of the TiO_2 films was determined by X-ray diffraction (XRD). The accelerating voltage and the applied current were 35 kV and20 mA, respectively. The surface morphology of the TiO_2 films were observed using scanning electron microscopy with an accelerating voltage of 20 kV. The thickness of the films was measured by using the Step Profilometer. Spectroscopic analysis of the TiO_2 films were performed using UV–Vis spectrophotometer (Hitachi, U-3210) with wavelength range of 200–900 nm. The solid was heated at various temperatures and these samples were characterized by XRD, and surface area [31].

RESULTS AND DISCUSSION

Variation of Viscosity of the Sol With Time

At room temperature the change in the viscosity of the precursor sol with time was studied using a viscometer. After sol dilutions the change in viscosity was observed which was found concentration dependent. The viscosity was very low initially but attained highest value within 15-36 hrs [fig. 2].

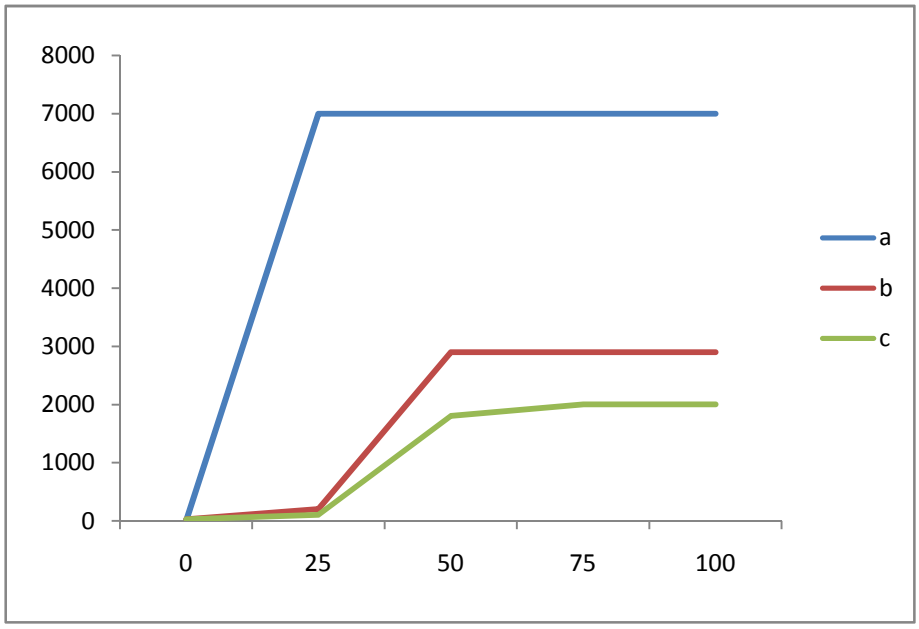

Fig. 2. Variation in viscosity with time of titanium peroxide sol having titanium ion concentration: (a) 0.01, (b) 0.005 and (c) 0.001 M.

Variation of Film Thickness with Viscosity

The viscosity plays an important role in the deposition process. The thickness of the films deposited at various viscosities was measured by the Profilometer. It was observed that the film thickness increases with increase in the viscosity of the precursor sol up to certain limit, i.e. in between 4000 and 12,000 cps. The films deposited using Ti-precursor sol of viscosity less than4000 cps were having different colors at different spots which indicates that the film deposited was very thin and non-uniform [fig 3]. The films deposited above 12,000 cps were reported to be thick and non-uniform [5].

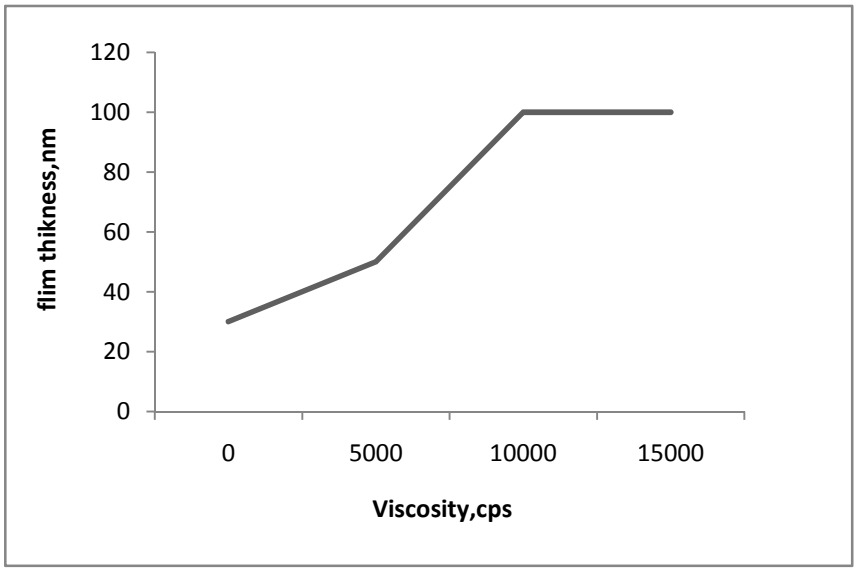

Fig. 3. Variation of film thickness with viscosity of sol

Characterization of Films

The thickness of the Ti (IV) oxide films on glass, silica and stainless steel plates was measured by the 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. 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.

CONCLUSION

A very simple method for the deposition of thin films of TiO_2 on various substrates like glass plates, silica 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. The films heated at various temperatures (from 200 to 600 $^{\circ}$C) are mostly of pure anatase type. The films heated at 400 $^{\circ}$C show excellent photocatalytic activity for the complete decomposition of various dyes in water like methyl orange, methylene blue.

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REFERENCES

[1] Fujishima, K. Honda, *Nature* , **1972**, 238, 37.
[2] Z. Ding, X. Hu, P.L. Yue, G.Q. Lu, P.F. Greenfield, *Catal. Today* **2001**, 68, 173–182.
[3] G. Pecchi, P. Reyes, P. Sanhueza, J. Villasenor, *Chemosphere* **2001**, 43, 141–146.
[4] R.S. Sonawane, S.G. Hegde, M.K. Dongare, *Mater. Chem. Phys*. **2002**, 77, 744–750.
[5] S. Sakka, T. Yoko, in: J.C. Jørgenson, R. Reisfield (Eds.), Chemistry, Spectroscopy, and Application of Sol–Gel Glasses, Springer, Heidelberg, **1991**, pp. 89–91.
[6] J. Yu, X. Zhao, G. Zhang, Han J., Zhao Q.: *Materials Science* **2001**, 1, 16.
[7] M. Andriainarivelo, R. Corriu, P. Mutin, A. Vioux: *Chem. Mater*. **1997,** *9*, 1098.
[8] H. Dislich, E .Hussmann: *Thin Solid Films* **1981**, *77*, 129.
[9] A Makishima, M. Asami, Wada K.: *J. Non-Cryst.Solids* **1990**, 121, 310.
[10] P. Baudry, A. Rodrigues, M. Aegerter: *J. Non-Cryst.Solids* , **1990**, 121, 319.
[11] Orel, M. Macek, A. Surca: *Proc. SPIE* **1994**, *2255*, 273.

[12] Orel, U. Lavrencic, M. Hutchins, K. Kalcher: *J.Non-Cryst. Solids* **1994**, 175, 251.
[13] A Hagfeldt, N. Vlachopoulos, S. Gilbert, Gratzel M.:*Proc. SPIE* **1994,** 2255, 297.
[14] M. Stromme, A. Gutarra, G. Niclasson, C. Granqvist*: J.Appl. Phys*. **1996**, 79, 3749.
[15] J. Bell, J. Barczynska, L. Evans, K. McDonald: *Proc.SPIE* **1994**, 2255, 324.
[16] H. Schroeder: *Physics of Thin Films* **1969**, 5, 123.
[17] B. Yoldaz: *US Patent* **1982**, 4 361 598.
[18] B. Yoldaz, O'Keefe T.: *Appl. Opt*. **1984** 23, 3638.
[19] Thomas: *Appl. Opt*. **1987**, 26, 4688.
[20] P. Biswas, D. Kundu, Ganguli D.: *J. Mater. Sci. Lett*. **1989**, 8, 1436.
[21] H. Floch, J. Priotton: *Thin Solid Films* **1989**,175, 173.
[22] Brinker, M. Harrington: *Sol. Energy Mater*. **1981**,5, 159.
[23] A Atta, P. Biswas, D. Ganguli: *J. Mater. Sci. Lett*. **1993**,12,760.
[24] T. Nishide, M. Shinoda: *Thin Solid Films* **1994**, 238, 163.
[25] B. O'Regan, J. Moser, M. Anderson: *J. Phys. Chem*. **1990**, 94, 8720.
[26] H. Pulker, G. Paesold, E. Ritter: *Appl. Opt*. **1976**, 15, 2986.
[27] Matthews, P. Infelta, M. Gratzel: *Sol. Energy Mater.Sol. Cells* **1996**, 44. 119.
[28] Z. Krejèová, P. Mecner, Z. Strnad, I. Hollerová, P. Pech: *Skláø a keramik* **2002**,52, 81.
[29] H. Tada and M. Tanaka, Langmuir, **1997**, 13, p. 360.
[30] L. Hu, T. Yoko, H. Kozuka, S. Sakko, *Thin Solid Films* **1992**, 219,18–23.
[31] N. Serpone , *J .Phys . Chem*. **1995,** 99, 16646