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Room temperature chemical deposition of amorphous TiO_2 thin films from Ti(III) chloride solution

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TiO_2 has been one of the most extensively studied oxides because of its remarkable optical and electronic properties. TiO_2 film in anatase phase could accomplish the photocatalytic degradation of organic compounds under the radiation of UV. It has many application prospects in the field of environmental protection such as sterilization and sewage disposal. Recent interest is focused on an amphiphilic TiO_2 surface induced by UV irradiation, which is expected to be applicable to a windshield and a mirror for vehicles [1]. On the other hand, in the field of alternative energy, a dye-sensitized solar cell is now a hot topic due to its high conversion efficiency produced with a porous TiO_2 electrode that is composed of few tenths of nanometer-sized particles [2, 3]. TiO_2 film with rutile phase is known as a good blood compatibility material and can be used as artificial heart valves.

From the point of view of practical use, the fixation of TiO_2 onto a substrate is very important and some methods to fix the TiO_2 particles have been developed. Consequently, a low-cost preparation and fixation of the TiO_2 photocatalyst with nanosized particle is necessary for practical applications. Many deposition methods such as thermal and anodic oxidation of titanium, electron beam evaporation, chemical vapor deposition, plasma enhanced chemical vapor deposition, reactive sputtering, sol-gel, spray pyrolysis etc have been reported to prepare nanometer-sized particle powder or thin films [4].

Recently, much emphasis has been put on the soft solution chemical processes for the preparation of advanced inorganic materials such as perovskite-type oxides, spinel-type oxides, superlattices and nanodots with quantum size effects. These low cost processes have been used in environmentally benign conditions. Therefore, these soft solution chemical processes are important for the preparation and fixation of the TiO_2 particles. Such processes include sol-gel, atomic layer deposition, electrochemical deposition, spray pyrolysis, dip coating, solution hydrolysis etc.

The TiO_2 nanoparticles have been prepared by chemical method using hydrolysis of $TiCl_4$, $Ti(SO_4)_2$, and TiI_4 [4–7]. The $TiCl_4$ was slowly dropped in deionized water at 273 K to get TiO_2 particles. Whereas $Ti(SO_4)_2$ solution was dropped in aqueous ammonia solution under stirring to get TiO_2 powder. Barringer and Bowen [8] prepared submicron TiO_2 powders by controlled hydrolysis of an alcoholic solution of $Ti(OC_2H_5)_4$ or $Ti(i\text{-}OC_3H_7)_4$, and showed that these powders gave sintered bodies with fine-grained microstructure and high density of a low sintering temperature. Kato *et al.* [9] synthesized spherical TiO_2 powder from an aqueous solution of $TiO(SO_4)$ by homogenous precipitation using urea as the precipitating agent at 343–363 K. The reports to produce TiO_2 films from chemical hydrolysis method are scanty in the literature. Transparent nanocrystalline anatase TiO_2 films were deposited on to conducting glass substrates from titanium tetraisopropoxide colloidal solution [10, 11]. In order to increase film thickness, the anatase TiO_2 films were treated with $TiCl_4$ solution for few hours and annealed at high temperature. The TiO_2 film thickness was typically 4 to 8 micron. For photosensitization studies, the TiO_2 coated glass was heated at 623 K for 30 min. Vigil *et al.* [12] have deposited TiO_2 films using microwave heating on glass and fluorine doped tin oxide coated glass substrates.

In the present investigation, chemical deposition of TiO_2 films at room temperature was carried out from titanium(III) chloride, $TiCl_3$ (Aldrich, USA) solution. As received $TiCl_3$ (20–30 wt% in HCl) solution was taken into the beaker and its pH was adjusted between 2–5 using 7% $NaHCO_3$ solutions with constant stirring. Deposition of TiO_2 films was carried out onto previously cleaned ITO coated glass substrates. The sheet resistance of ITO coated glass substrate was between 30–40 ohm/cm^2. The substrates were cleaned with detergent solution and ultrasonically before use. The TiO_2 films were taken out of the bath after deposition period of 1–6 h, washed with water and dried under argon flow. The TiO_2 films were heat treated in air at 723 K for 1–12 h.

Thin films of TiO_2 were characterized using following techniques. The X-ray diffraction (XRD) patterns were obtained by using X-ray diffractrometer (RINT/PMAX 2500, Rigaku, Japan). Micro structural studies were carried out with scanning electron micrographs, obtained with FE-SEM, (SM-6340F, Jeol, Japan). The optical absorption studies were carried out with UV-VIS spectrophotometer (Varian-Cary 100, Australia). Photoactivity was studied by forming a photoelectrochemical cell with TiO_2 as a photoelectrode and platinum spiral wire as a counter electrode. The electrolytes used were 1 M NaOH (pH = 12) and 0.1 M sodium acetate (pH = 7.2). A Xe lamp (450 W,

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Thermo Oriel Co., USA), with illumination intensity of 100 mW/cm^2 at 300 nm wavelength was used as a light source.

Preparation of powder and thin films of various metal chalcogenides including oxides have been reported by chemical or controlled precipitation method. In this method, reaction takes place between dissolved precursors generally in aqueous solution at low temperature. When the solution is saturated, the ionic product is equal to solubility product and when it exceeds, precipitation occurs and ions combine on the substrate and in the solution to form nuclei. Generally metal ions are complexed and chalcogen ions are chosen in such a way that a reaction takes place between slowly released metal ions to form product in powder or thin film form. Depending upon deposition conditions such as bath temperature, stirring rate, pH, solution concentration etc, the film growth can take place by ion-by-ion condensation of materials or by adsorption of colloidal particles from solution on the substrate.

In the present case, TiO_2 films have been deposited on ITO coated glass substrate by slow hydrolysis of $TiCl_3$ solution. Rotzinger and Gratzel [13] have reported on the kinetics of decomposition of $TiCl_3$ solution. Reaction of Ti(III) with O_2 is rate determining step in TiO_2 formation. The $TiOH^{2+}$ is the only reactive species as per the reactions;

$$Ti^{3+} + H_2O \rightarrow TiOH^{2+} + H^+ \tag{1}$$

and

$$TiOH^{2+} + O_2 \rightarrow TiO_2 + 2OH^- \tag{2}$$

The reaction (1) should have rapid pre equilibrium.

The pH of $TiCl_3$ was varied between 2–5 with addition of $NaHCO_3$ solution. It was found that with increasing pH, rate of hydrolysis was increased resulting into TiO_2 precipitate formation in bulk of solution without film formation on the substrates. The suitable pH range was found to be 3–3.5. The TiO_2 film formation stared within about 30 min and completed within 6 h at room temperature (296 K). The solution color changed from violet-blackish to whitish after six h and further dipping of substrate into bath resulted in dissolution of deposited TiO_2 and ITO coating on the substrate in the solution. The TiO_2 film thickness was typically between 10 to 50 nm, depending upon solution pH and deposition time. The TiO_2 films were thin, specularly reflecting, and well adherent to the ITO coated glass substrate.

TiO_2 exists in three different phases: anatase, rutile and brooklite. However, only anatase and rutile and amorphous films of TiO_2 have been reported [14]. The influence of annealing temperature on the properties of magneton sputtered TiO_2 films has been studied by Hou *et al.* [15]. Annealing temperatures until 500 °C showed weak peaks due to anatase phase.

Film crystallinity was analyzed using X-ray diffraction. Practically no difference was observed between XRD corresponding to ITO coated glass and corresponding to the as-deposited TiO_2 film on ITO coated glass substrate, which indicates very low crystallinity and amorphous characters. The TiO_2 films were heat treated at 623 K for 12 h. In Fig. 1, spectra are shown corresponding to the heat-treated TiO_2 films on ITO coated glass at two different thicknesses (10 and 50 nm). The similarity between them shows that amorphous character practically does not change. Only peak intensity of ITO material was reduced with thick TiO_2 film. Similar results have been reported for TiO_2 films deposited from microwave-activated solutions [12].

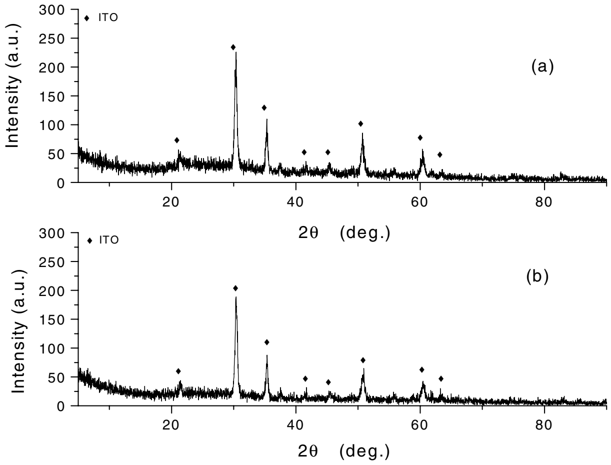
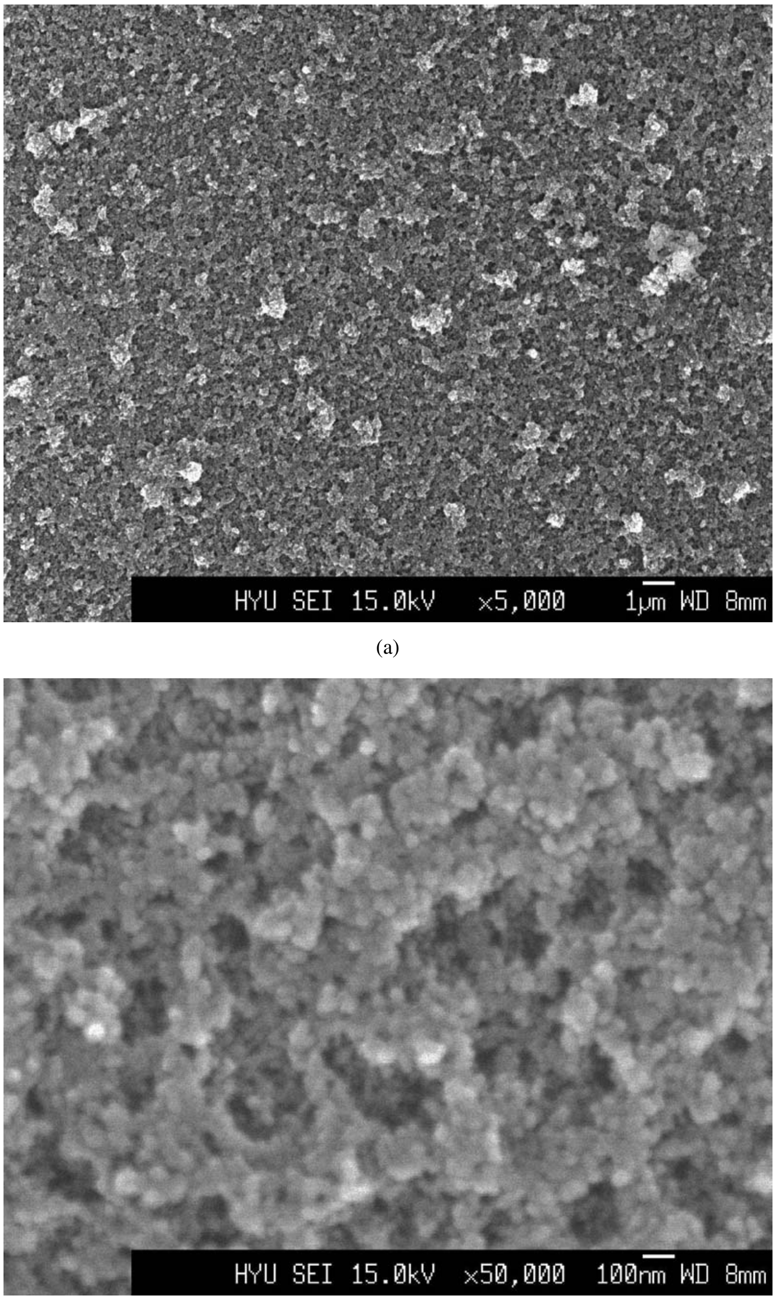


Figure 1 The XRD patterns of TiO_2 films deposited on ITO coated glass substrates at two different thicknesses: (a) 10 nm, and (b) 50 nm. The films were heat treated at 623 K for 12 h.

Scanning electron micrographs of TiO_2 film on ITO coated glass substrate at two different magnifications (5 000× and 50 000×) are shown in Fig. 2a and b. At 5 000× magnification, a well covering and rough TiO_2 film surface is seen. At high magnification, a TiO_2 film with porous structure is clearly visible, similar to those of other chemical methods such as sol-gel, spray pyrolysis, dip coating etc.

Optical absorption spectrum of TiO_2 film on ITO coated glass is shown in Fig. 3. The TiO_2 film show sharp increase in absorption below 350 nm. A tailing absorbance in visible region of 400 to 500 nm was observed. A similar absorbance has been observed for the TiO_2 films obtained with hydrolysis of $TiCl_4$ [9] and electrodeposition [16]. Serpone has attributed the visible absorption of TiO_2 films to the charge-transfer transition from Cl^- to Ti(IV) [17], whereas Justica *et al.* [18] have attributed this to the presence of an electronic band due to defect states close to the conduction band for sub-stoichiometric TiO_2 material.

Application of TiO_2 in photocatalysis is well known. Dye-sensitzed photoelectrochemical cell systems based on highly porous nanocrystalline films of TiO_2 are of considerable interest because of their demonstrated high-power conversion efficiency (7–9%), potential low cost, and high semiconductor stability. The most extensively studied system consists of a monolayer of a Ru-bipyridyl based charge transfer dye adsorbed onto the surface of a thin nanocrystalline TiO_2 thin film supported on ITO coated glass. The TiO_2 is stable in many electrolytes and TiO_2 based photoelectrochemical and photoelectrolysis cells in different electrolytes such as KOH, NaOH, KCl, Na_2SO_4-NaI, H_2SO_4, $K_3FeCN_{6'}$ etc. [1, 2, 8] have been studied.



(a)

(b)

Figure 2 Scanning electron micrographs of TiO_2 film at two different magnifications: (a) 5 000× and (b) 50 000×.

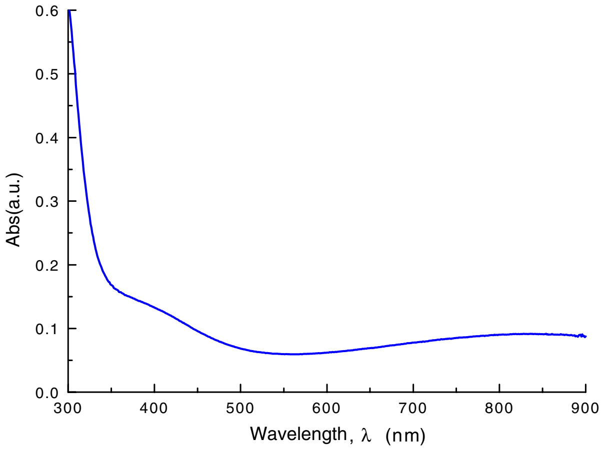


Figure 3 Optical absorption spectrum of TiO_2 film deposited on ITO coated glass substrate.

In order to demonstrate the potential use of chemically deposited TiO_2 films, photoactivity of TiO_2 thin films in electrolytes such as 1 M NaOH and 0.1 M Na-acetate electrolytes was studied. Fig. 4a and b shows I–V characteristics for TiO_2 film deposited on ITO coated glass substrate under chopped light condition. The film showed photoactivity with n-type behavior. In both cases, the dark current is nearly equal to zero. The photocurrent obtained was of the order of microamp/cm^2. The low photocurrents have been attributed to high bandgap (>3.2 eV) and amorphous structure (as evidenced by XRD studies) of TiO_2 films and series resistance offered by ITO coated glass substrate. It exhibited better photocurrent in Na-acetate than in NaOH electrolyte. However, the flat band potential, V_{fb} was found to ∼−500 mV (Ag/AgCl) in both electrolytes.

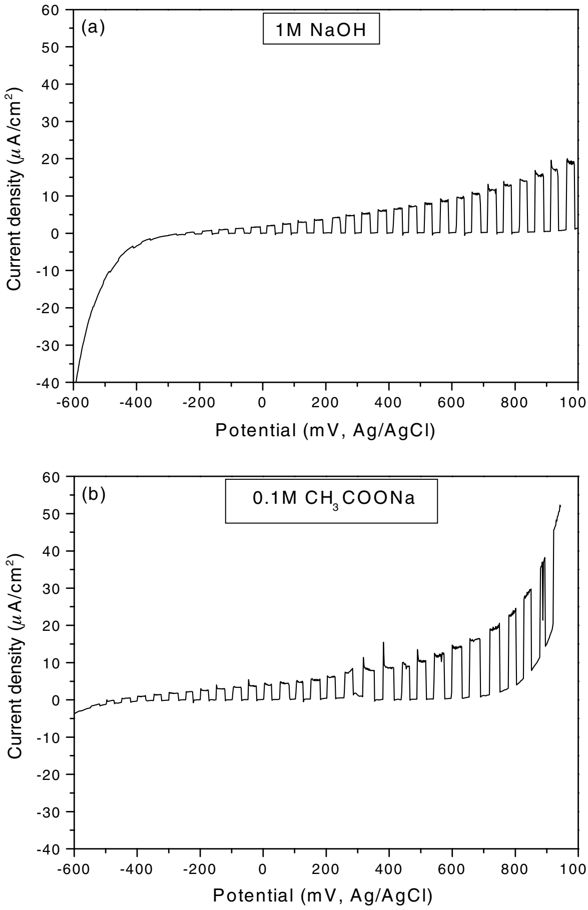


Figure 4 The current-voltage (I–V) characteristics of TiO_2 film deposited on ITO coated glass substrate in (a) 1 M NaOH, and (b) 0.1 M sodium acetate electrolytes. The light was chopped during illumination.

In conclusion, TiO_2 thin films have been grown onto ITO coated glass substrates using room temperature chemical deposition method from $TiCl_3$ solution. The samples obtained are well adherent and amorphous. The following advantages have been found for the method described: it is simple, it uses low temperatures (less then 300 K), layers are grown in a relatively short time, thickness control is possible through pH of solution and deposition time. The TiO_2 films are porous and exhibit photoactivity. These widen the technological uses of chemically deposited TiO_2 films.

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