Study of gradual variation of structural, surface morphological and photocatalytic properties of sol-gel derived transparent TiO\textsubscript{2} thin film

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Abstract. In this study, an effort has been made to prepare TiO\textsubscript{2} thin films by sol-gel technique with small variation of PEG to observe the gradual change of structural, optical and surface morphological properties. The X-ray diffraction study indicates that increase of PEG content enhances crystallite size but the density of crystallite is reduced. The structural, optical and surface morphological study reveals that sol gel derived TiO\textsubscript{2} thin film with small variation of PEG can achieve gradual change from dense random structure to early stage of porous network structure. The crystallite size, grain size, porosity and surface roughness can be efficiently modified with the small variation of PEG content.

1. Introduction
Over the past few years, titanium oxide (TiO\textsubscript{2}) has attracted much attention because of its various photodriven applications, such as photocatalytic, photovoltaic, photochromatic and photoinduced superhydrophilical applications etc. \cite{1}. However regarding the different physical and chemical properties of TiO\textsubscript{2}, each application has its own requirement \cite{2-4}. So according to the requirement of the application, TiO\textsubscript{2} is needed to be modified. On the other hand, in some special cases, single TiO\textsubscript{2} thin film is needed to be used for two different separate applications, when a compromise between specific requirements is necessary \cite{3}. It is therefore very important to study the evolution of different physical and chemical properties of TiO\textsubscript{2}, prepared by a suitable technique which is effective for controlled modification.

Among the various techniques to prepare TiO\textsubscript{2} in immobilized form the relatively simple and inexpensive sol gel method is the most widely used because of its ability to obtain films with tailored properties on large, curved substrates. Preparation of TiO\textsubscript{2} film from alkoxide solution via dip coating technique has been studied for a long time, where metal alkoxide precursor is hydrolyzed under controlled conditions to form an extensive three dimensional network of linked TiO\textsubscript{6} octahedra \cite{5}. Recently polyethylene glycol (PEG) has been widely used as a template to modify the structure and surface morphology of the TiO\textsubscript{2} thin film, which was initially reported by Vong et al \cite{6}. However most of these works emphasize on the use of optimum amount of PEG to get large modification. In our present study, TiO\textsubscript{2} thin films have been prepared on glass substrate by sol-gel technique with a very small variation in the amount of PEG concentrations in order to study the gradual change in the
structural, optical and surface morphological properties. Finally, the effect of modifications has been tested by the measurement of photocatalytic ability.

2. Experiment

Tetrabutylorthotitanate (TBOT), diethanolamine (DEA) and absolute ethanol were used as starting materials. 8 ml of TBOT and 3 ml of DEA were dissolved in 35 ml ethanol to prepare the precursor solution. After stirring for 2 h at room temperature, a mixed solution of water and ethanol in the ratio of 1:10 was added drop wise. Finally, 0.2 gm and 0.3 gm of PEG (2000) were respectively added to the 100 ml of above solutions. The resultant alkoxide solution was stirred at room temperature for hydrolysis reaction for 2 h. The films were formed on the glass substrates from TiO\textsubscript{2} sol by dipping and withdrawing in an ambient atmosphere. The withdrawal speed was 2 mm/sec. The substrates coated with gel films were dried at 60\degree C before calcined at 550\degree C for 1 h. The thickness of the TiO\textsubscript{2} films was adjusted by repeating the cycle from dipping to heat treatment for 8 times.

The thicknesses of the TiO\textsubscript{2} thin films were about 700 nm - 800 nm, measured by DEKTAK surface profiler. The crystallization behaviour was monitored by a TG-DTA machine (Seiko Instruments SSC/5200). The crystal structures of the TiO\textsubscript{2} films were determined by X-ray diffraction analysis with Cu-K\alpha. The optical properties of the films were measured with Jasco V-550 spectrophotometer at room temperature. The Surface characteristics were analyzed using field emission scanning electron microscope (FE-SEM) (JEOL, FE-SEM 6700) and atomic force microscope (AFM) (SHIMADZU SPM-9500J2). The photocatalytic decomposition of methanol (5 \mu L) was evaluated by (FTIR, JASCO 480 plus) measuring its concentration decay of methanol on TiO\textsubscript{2} films was carried out under irradiation of UV-visible wavelength of 300 nm - 760 nm.

3. Results and discussion

In the Fig. 1 the XRD spectra of TiO\textsubscript{2} film, prepared without PEG, shows anatase phase with good crystallinity. Fig. 2 (inset) shows the TG-DTA curves for the TiO\textsubscript{2} gel prepared with 0.3 gm as a function of temperature. Two small exothermic peaks at about 280\degree C, 334\degree C and a very sharp exothermic peak at 540\degree C are ascribed to hydration and combustion of organic substance and the
crystallization to anatase phase, respectively. With the increase of PEG content the intensity and the number of peak related to anatase phase decreases. However, the crystallite sizes derived with Debye–Scherrer’s equation using the anatase peak (220) are 12.3 nm, 12.8 nm and 13.3 nm for the TiO\textsubscript{2} thin film, deposited without PEG and with 0.2 gm, 0.3 gm of PEG respectively. The XRD result indicates that the TiO\textsubscript{2} thin film without PEG has more compact structure with high density of crystallite. While for TiO\textsubscript{2} film with the same number of coatings, introduction of PEG induces porous structure with less number of crystallites. Interestingly, the presence of PEG doesn’t inhibit the crystallization but on the contrary it helps the growth process.

In the Fig. 2, the absorption spectrum of TiO\textsubscript{2} thin films reveals definite shift of absorption edge to the higher wavelength with the increase of PEG content and the average absorbance is also higher for higher PEG content. TiO\textsubscript{2} is an indirect band gap semiconductor, i.e. TiO\textsubscript{2}, a plot of $(\alpha h\nu)^{1/2}$ vs photon energy reveals the optical band gap of the material, where $\alpha$ is absorption coefficient. The deduced optical band gap decreases from 3.19 eV to 3.15 eV due to the effect of addition of PEG.

The refractive index of the thin film ($n_\lambda$) is calculated from the optical transmittance data using the Swanepoel's envelope method [7] are 2.42, 2.32 and 2.24 respectively for the TiO\textsubscript{2} thin film deposited without PEG and with PEG of amount 0.2 gm and 0.3 gm. The variation of porosity of the thin film, indicated in Fig. 3, has been determined from the value of refractive index [8]. It reveals that with the increase of PEG up to 0.3 gm the porosity increases to 25%. Similar kind of enhancement is also observed in the variation of rms roughness, revealed from AFM measurement.

The surface structure of the TiO\textsubscript{2} thin film prepared without PEG, indicated in the SEM image in Fig. 5(d), shows scattered grain clusters in the large area of small continuous grains. The introduction of 0.2 gm of PEG induces granular structure of similar size of grain clusters with distinct cluster boundaries and separation between the clusters become prominent. The use of 0.3 gm of PEG enhances these effects and it shows the sign of early stage of porous network structure. The formation of porous network structure is due to the fact that the sol particles formed by the sol–gel reaction were covered by PEG chains to form an inorganic/polymer composite. While calcined under high temperature, PEG was demolished from the composites and left a porous network. The AFM image of the sample corresponding to 0.3 gm PEG shows uniform grain clusters, when vertical scale takes
higher value, which indicates higher roughness of the surface.

The detailed description of photo-decomposition of methanol has been described else where [9]. IR-anti symmetric stretching band of CO$_2$ at 2340 cm$^{-1}$ was assigned for the confirmation of photo-decomposition of methanol [10]. The photocatalytic activity improves with the increase of PEG content, indicated in Fig. 4. It is may be due to the fact that enhancement of PEG content increase the crystallite size, induce porosity and make the surface rough with more open surface [11].

4. Conclusions

TiO$_2$ thin films were prepared on glass substrate by sol gel dip coating technique with small variation of PEG concentration to study the gradual change of the structural, optical and morphological properties. The study of X-ray diffraction reveals that introduction of PEG enhances the crystallite size while it reduces density of the crystallite than the TiO$_2$ film of same thickness, prepared without PEG. From the structural study it has been observed that PEG induced modification is a gradual change from dense, random structure to a early stage of porous network structure, where porosity and roughness increases continuously. Optical study reveals that in this limit of PEG concentration optical band gap decreases with the increase of PEG content.

References

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