Synthesis and Characterization Of TiO_2 Nanocrystalline Thin Films Via Dip Coating Technique Towards the Applications of Photocatalytic Activity

S.Prathiba Ponmary
Department of Physics
Hindustan University
Chennai- 603103, Tamil Nadu, India

Suganthi Devadason
Department of Physics
Hindustan University
Chennai- 603103, Tamil Nadu, India

***Abstract*— Titanium dioxide (TiO_2) is one of the most important multifunctional metal oxides that has been widely examined for its versatile applications in environmental purification and solar energy conversion. Titania has proved to be a very important photocatalyst because of its strong oxidizing power, nontoxicity, and long-term photostability. In the present work, TiO_2 nanocrystalline films were prepared using dip coating technique for two different molar concentrations of the precursor solution, namely 0.08 and 0.12M. The prepared samples were characterized for studying the structural and optical behavior using X-Ray Diffraction (XRD), UV-visible and Photoluminescence (PL) spectroscopy. From the XRD studies, it is found that the average crystallite size is lesser for film prepared with higher molar concentration. The calculated energy band gaps of films from a molarity of 0.08 and 0.12 are deduced as 3.43 and 3.14 eV, respectively. The emission peak of the PL spectra has a lesser intensity for a higher molarity film which is more favorable for exhibiting photocatalytic activity.**

Keywords*— Nanocrystalline, Titanium dioxide, Dip coating, Photocatalytic activity, Thin films

I. INTRODUCTION

Among various semiconductors, TiO_2 is proved to be the most suitable catalyst in view of its strong oxidation activity. It has excellent chemical, physical, optical and electric properties i.e., high chemical stability, non-toxicity, high thermal stability, redox and photoabsorption properties [1]. TiO_2 is synthesized by different methods such as sol-gel, hydrothermal etc [2]. TiO_2 is one of the most widely studied materials for its use in solar cells, pollutant degradation, photolysis of water, gas sensor and bio-applications. This paper deals with the synthesis of nanocrystalline TiO_2 thin film using dip coating by optimizing the molarity of Titanium tetraisopropoxide (TTIP) and analyzing structural and optical studies.

II. EXPERIMENTAL TECHNIQUE

The nanocrystalline TiO_2 thin films were prepared at room temperature by hydrothermal method using dip coating technique. In a typical synthesis method, a precursor solution was prepared by mixing appropriate ratios of TTIP/ Ethanol/ Con.HCl as 0.08M: 15M: 0.05M. After stirring for two hours, a small amount (20 μl) of PEG 300 was added to change the structure of thin film to mesoporous one [3]. Then the solution was stirred for 12hr at room temperature to improve the porosity of the film. The obtained solution were dip coated onto a clean glass substrate for 12 dips. The prepared samples was annealed at 400 ˚C for 1 hr. The same process is repeated by changing the molarity of TTIP as 0.12 and maintaining the total dips as 12

III. RESULTS AND DISCUSSION

A. Structural Analysis

Shimadzu XRD-6000 was used to record the X-Ray Diffraction pattern which is shown in figure 1. The sharp peak is attributed to the crystalline nature of the samples. The prominent peaks for samples is 32 ˚ (JCPDS # 720021 and # 841750) which refers to (111) plane of titanium dioxide. The crystallinity of 0.12M is good as compared with 0.08M respectively. Thus diffraction pattern peak intensity is enhanced for increased molarity i.e. 0.12M. The molarity increment can improve the absorbance of TiO_2 by relating it with high density of TiO_2 particles [4]. The average crystallite size of the prepared nanocrystalline thin film was calculated from XRD spectra using Debye–Scherrer's equation,

$$D=0.94\lambda/\beta\cos\theta \text{ -----------------(1)}$$

Where λ= X-Ray wavelength, β= Full width half maxima (FWHM), θ= Bragg's angle

The calculated result was found to be 30 and 20 nm for 0.08 M and 0.12 M. Thus average crystallite size decreases with increased molarity.

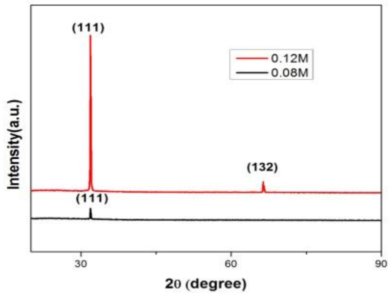

Figure 1. XRD pattern of sample 0.08 and 0.12M

B. Optical Studies

The absorbance spectra was recorded using Jasco V-670 Spectrophotometer and is shown in Figure 2. The High molarity concentration of TiO_2 can produce a much thicker thin film leading to the absorption of more photon energy resulting in increased the absorbance value in the visible region (358 nm for 0.12 M).

The band gap energy along the fundamental absorption region is determined by the following method.

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \text{-----------------(2)}$$

Where, d is the thickness of the sample, T is the transmittance and α is the absorption coefficient.

The values obtained for α in the absorption region is then analyzed using the relation $\alpha E = A(E - E_g)^{1/2}$ where A is a constant.

The value of Eg is found using graph drawn between (αE)2 and E. Typical plots of (αE)2 versus E are shown in figure 3. The extrapolation of the linear portion to the energy axis gives the value of bandgap energy E_g.

It is found that the absorption edge is shifted towards the higher wavelength as the molarity increases. The energy band gap (E_g) of the films can be estimated by plotting (αhν)2 versus hν , then extrapolating the straight-line part of the plot to the photon energy axis is shown in figure 3 and 4 respectively.. The energy band gap for the prepared films of two different molarity (0.08 M and 0.12 M) was found to be 3.42 and 3.14 eV respectively.

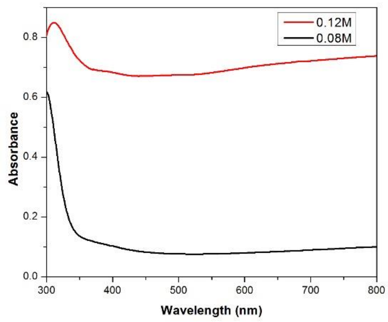

Figure 2. Absorption spectra of samples 0.08 and 0.12M

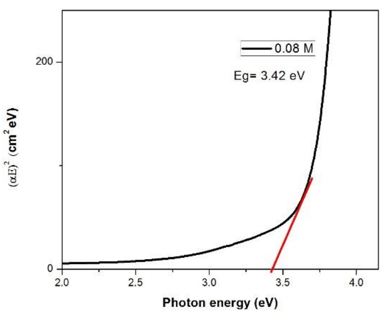

Figure 3. Energy band gap of sample 0.08M

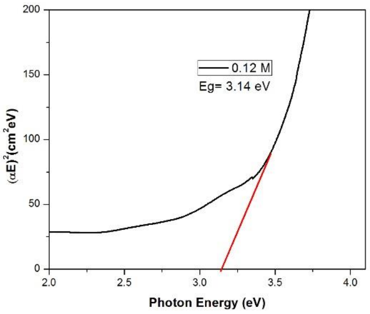

Figure 4. Energy band gap of sample 0.12M

The photoluminescence (PL) study was taken using Horiba Jobin Yuon Fluorg spectrophotometer which is shown in figure 5. PL has been widely used to study the efficiency of charge carrier trapping, immigration, and transfer behaviors of the photoexcited electron–hole pairs in semiconductors. Since the PL emission comes from recombination of excited electrons and holes, the lower PL intensity indicates a lower recombination rate of electron–hole under the light irradiation, which may also imply a higher photocatalytic activity of the modified TiO_2 [5]. In the present work the PL emission spectra was taken for excitation wavelength, λ=350 nm. The prominent PL emission peak is observed in blue region. There is a splitting of the emission maximum observed with the bands centered on 415 nm and 439 nm in emission spectra of the samples. This may be due to the emissions from the spin–orbit split-up neighbouring excited states. When the molarity of the TTIP increases the recombination rate of electron- hole is reduced. Thus lower the intensity, sample is favorable for photocatalytic activity (0.12M).

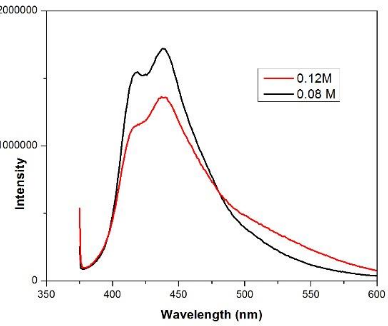

Figure 5. PL spectra of sample 0.08 and 0.12M

IV. CONCLUSION

In this present work TiO_2 nanocrystalline thin films were prepared by dip coating technique by optimizing the molarity of TTIP. From XRD studies it is found that average crystallite size decreases with increased molarity. The absorbance spectra reveals that the absorption edge is red shifted for higher concentration and the energy bandgap is red shifted for higher molarity. The emission peak of the PL spectra has a lesser intensity for a higher molarity film which is more favorable for exhibiting photocatalytic activity.

V. ACKNOWLEDGMENT

The authors gratefully acknowledge Hindustan University for giving instrumentation facilities and Karunya University for providing characterization facilities.

REFERENCES

[1] Md. Abdulla-Al-Mamun, Yoshihumi Kusumoto and Md. Shariful Islam, J. Mater. Chem., 22, 2012, 5460,

[2] M. Malekshahi Byranvanda, A. Nemati Kharata, L. Fatholahib, Z. Malekshahi Beiranvandc, JNS, 3, 2013, 1-9

[3] T. Kitamura and H. Kumazawa. Chem. Eng. Comm., 192, 2005, 795–804

[4] Puteri Sarah Mohamad Saad, Hanis Binti Sutan, Shafinaz Sobihana Shariffudin, Hashimah Hashim and Uzer Mohd Noor, Materials Science and Engineering, 99, 2015, 012006.

[5] Kuang-I Liu, Chung-Yi Su and Tsong-Pyng Perng, RSC Adv., 5, 2015, 88367