Synthesis of Cadmium Sulfide Nanoparticle on TiO_2 Electrode by SILAR and their Possible Application in TiO_2 based Photoelectrochemical Device

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Abstract: Nanostructured CdS thin film have been deposited on TiO_2 thin films prepared by sol-gel process over ITO coated conducting glass substrate. Growth of nanostructured CdS thin film on TiO_2 matrixes have been carried out via Selective ion layer adsorption and reaction technique(SILAR). The synthetic procedure of CdS thin film as well as structural, optical and photoelectrochemical properties of TiO_2/CdS composite photoelectrodes are demonstrated. The structure and morphology of TiO_2/CdS composite photoelectrodes have been analyzed using SEM and XRD experimental techniques. The photoelectrochemical behavior of TiO_2/CdS composite photoelectrodes has been established on the basis of current-voltage studies under dark and under illumination experimental conditions.

Keywords: quantum dots, injection solar cell, titanium oxide, solgel, SILAR

Keywords: Selective ion Layer adsorption and reaction method(SILAR), TiO_2 thin film, nanostructured CdS thin film, Photoelectrochemical cell (PEC).

1. INTRODUCTION

Development of alternate (renewable) sources of energy is an important issue, which has attracted attention over the past decade. A major step towards the realization of this goal has been achieved by the development of solar, thermal, photovoltaic and photoelectrochemical (PEC) solar cells [1-2]. Studies involving solid-state materials for efficient and sustained conversion of solar energy into electricity still continue to be of immense contemporary relevance. In recent years, photoelectrochemical process at TiO_2 based semiconductor (SC) photoelectrode-electrolyte interface has received much attention because of their possible applications in the conversions of solar energy into electrical energy and especially in case of water splitting to generate environmental friendly fuels [3-4]. Choice of materials plays an important role for the fabrication of any photoelectrochemical cell [5-6]. For occurrence of effective charge transfer processes at the SC-electrolyte interface, i) the SC material must have a band gap between 1-3 eV so that it can

utilize the maximum visible part of solar spectrum ii) material must be stable against corrosion when placed in a specific redox system. TiO_2 shows good resistance towards corrosion but because of its large band gap (3.2 eV) [7-8] the overall conversion efficiency in visible region are not satisfactory. To overcome this problem number of process have been designed and tested to sensitize the TiO_2 photoelectrodes in visible region and the most common sensitizer used for this process are photosensitive organic dyes [9-10]. In spite of showing acceptable conversion efficiency, DSSC have also some drawback. Generally the dyes used in DSSC are photocorrosive in nature and therefore the overall conversion efficiency of this cell will also be going on hampered with time. So there is need to replace these photosensitive dyes with some other SC materials (e.g. narrow band gap SC quantum dots or nanostructured thin film sensitizer) which not only have good solar absorber in visible region but also shows some enhance resistance towards photocorrosion[11-13]. Various semiconductors QD's such as PbS [14], CdS [15], Bi_2S_3 [16], CdSe [17] and CdTe [18] have been successfully demonstrated as visible light sensitizer for TiO_2 based electrodes. However the main challenge in this field is still the development of synthetic methods by which one can prepare nanostructured SC material with desired morphology. Number of methods have been reported for the preparation of both QD's and nanostructured thin film sensitizers but unfortunately most of the methods are time consuming or required high temperature experimental conditions. Presently we are exploring the possibilities to modify TiO_2 particulate films with nanostructured CdS thin film sensitizer with an aim to tune the response of the photoelectrochemical cell in the visible region. The modification process has been carried out via following deposition of Quantum Dots by SILAR route. As deposited thin films has been characterized on the basis of SEM, and XRD studies for determination of their surface morphology, surface roughness and grain size. XRD and SEM study does reveals that as deposited different metal sulfide thin films is of nanodimensions in nature. Linear Sweep Voltametric study under dark and under illumination conditions confirmed the improved photoelectrochemical behavior of TiO_2/CdS composite material.

2. EXPERIMENTAL

2.1 Preparation of TiO_2 sol and thin films:

A 0.5 M TiO_2 Sol has been prepared by the partial hydrolysis and poly-condensation of titanium tetrabutoxide ($Ti(OC_4H_9)_4$) with water using isopropyl alcohol as a solvent and HNO_3 as catalyst. Formation of titanium oxide film on the glass substrate surface takes place as per the following reaction.

$Ti(OC_4H_9)_4 + 2H_2O \rightarrow Ti(OC_4H_9)_2(OH)_2 + 2C_4H_9OH$

$Ti(OC_4H_9)_2(OH)_2 + Ti(OC_4H_9)_2(OH)_2 \rightarrow Ti_2O(OC_4H_9)_2(OH)_2 + H_2O$

This reaction stops with the inclusion of two water molecules:

$Ti(OC_4H_9)_4 + 2H_2O \rightarrow TiO_2 + 4C_4H_9OH$

TiO_2 thin films were fabricated on the ultrasonically cleaned ITO glass substrate by the dip coating process at a withdrawal speed of 12 cm/min. After coating, the TiO_2 films have been dried at 60-70 ^oC and subsequently annealed at 450 ^oC for 1h as per the procedure described elsewhere.[19,20]

2.2 Assembling CdS quantum dots on the TiO_2 film surface:

CdS quantum dots has been attached to the surface of TiO_2 film by SILAR (Successive ionic Layer adsorption & reaction) method. Four beakers of 100ml capacity were taken, marked as I, II, III & IV and kept in line on the table sequentially. These beakers were filled with different solutions/solvents as; beaker No. I - 0.05 Molar $Cd(NO_3)_2$ solution in ethanol, beaker No. II - pure methanol; beaker No. III - 0.05 Molar Na_2S solution in methanol and beaker No. IV - pure methanol. TiO_2 thin film coated FTO glass substrate was sequentially & successively immersed in each solution for one minute with one minute gap in between. One dip in all the four beakers completes one cycle. Several such cycles were repeated to obtain varying densities of CdS quantum dots onto the TiO_2 film. After drying at room temperature these slides were sintered at 300°C in an electric furnace under atmospheric conditions for one hour.

2.3 Characterization of composite photoelectrodes

XRD measurements of as deposited composite materials were carried out with Bruker:D8 Advance Diffractometer which uses mono-chromatized CuKα radiations of wavelength (λ) = 1.5406 Å as probing radiations. The nanoparticle size and surface morphology was studied with high resolution Scanning Electron Microscope model LEO 440. Photoelectrochemical properties of thin film samples were studied on Eco-Chemie Model N302 electrochemical workstation in three electrode configuration with titanium foil as a counter electrode and a saturated calomel electrode (SCE) as refrence electrode in I_2/I^{3-} redox couple. Linear Sweep Voltametry experiments, under dark and under illuminated conditions, were performed. 200W tungsten lamp was usedas light source to illuminate the surface of working electrode.

3. RESULTS AND DISCUSSION:

3.1 Structural Studies

A typical X-ray diffraction pattern of pure TiO2 film on FTO glass substrate and TiO2 film with over layer of CdS nanoparticles by SILAR process (TiO_2/CdS) is shown in figure1. Major peak in the CdS nano-particle decorated electrode appears at 2θ value = 28.215 Å which corresponds to CdS. This peak is used to calculate the nano-particle diameter using Sherrer's formula as described below. Crystallite size of TIO2 This result clearly indicate that in as prepared composite

photoelectrode a layer of both TiO_2 and is calculated from XRD peak at 27.2 Å in TiO2 film XRD spectra which corresponds to 101 reflection in corresponding to anatase phase of the material

The average grain size of the composite materials were also estimated from the XRD patterns using the Scherrer's formula

$$d = \frac{0.89\lambda}{\beta \cos\theta_B} \quad (1)$$

where d is the average diameter of the composite material, λ is the wavelength of X-ray used (λ= 1.5406Å), β is the full width at half maximum of XRD peak and θ_B is Bragg angle for the particular peak. The average grain size was found to be ≈ 20 nm for CdS nano-particles and 17nm for the TiO_2 anatase phase crystallite.

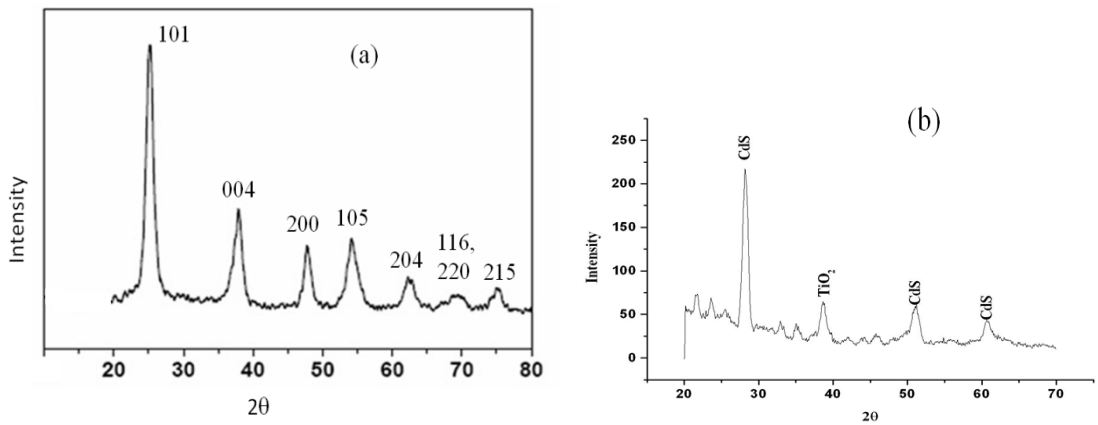

Fig.1: X-ray diffractograms of (a) pure TiO2 film and (b) TiO2 film with overlayer of CdS nano-particles.

3.2 Surface Characterization

The surface morphology and structure of as deposited TiO_2 thin film and composite TiO_2/CdS photoelectrode were also investigated using Scanning electron microscope (SEM). SEM is the promising experimental tool for the topography study of samples, as these studies gives important information regarding the growth mechanism, shape, size and surface roughness of the grains. Fig.2(a) represents surface morphology of TiO_2 thin film deposited on ITO coated conducting glass substrate. From the figure it has been clearly observed that small spherical nanosized TiO_2 particles are uniformly spread all over the glass substrate. Fig.2(b) shows SEM image of electrodeposited CdS thin film over TiO_2 matrix at conducting glass substrate. From the figure it is clearly observed

that surface morphology of as deposited CdS thin film is completely different from those of TiO_2 thin film Fig.2(a) indicating CdS possesses small wafers like structure randomly distributed over the entire TiO_2 matrixes. However size distribution of CdS nano-wafers are not uniform throughout the region.

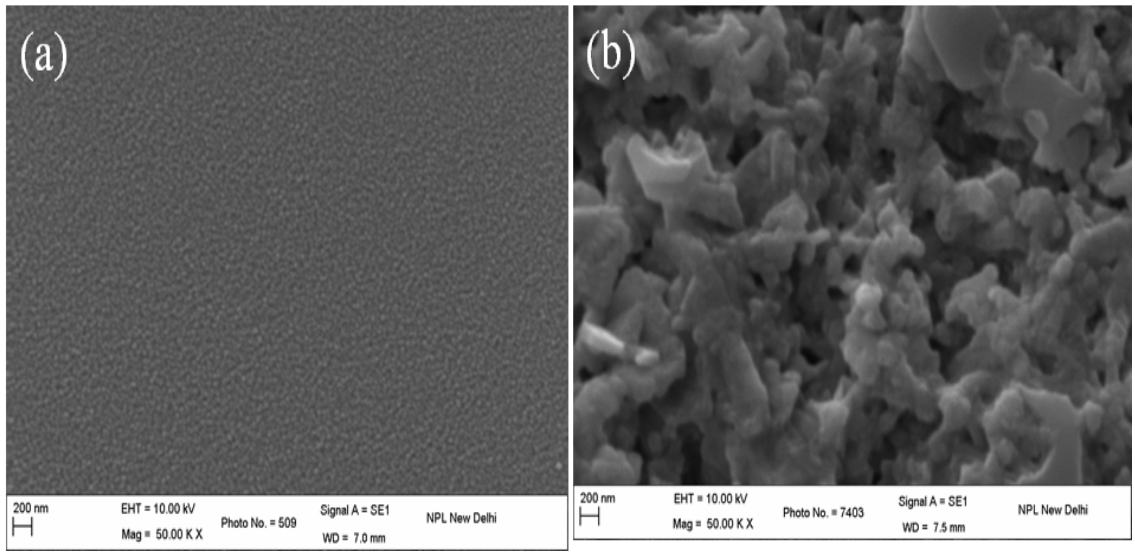

Fig.2: SEM micrograph of (a) Pure TiO2 film coated substrate surface and (b) TiO2 film covered with CdS nanoparticles

3.3 Photoelectrochemical Characterization:

The photoelectrochemical properties of TiO_2/CdS composite photoelectrode were studied using a three electrode system in $\mathbf{I^-/I^{3-}}$ redox system. Electrodes were illuminated from the as deposited semiconductor electrode side. Linear Sweep Voltamaograms of TiO_2/CdS composite photoelectrode under dark and illuminated conditions are shown in Fig.3. The voltamogram clearly shows that the CdS sensitized TiO_2 photoelectrode generated much higher photocurrent response as compared to the unsesitized TiO_2 film. This comes from the fact that the nanostrutured CdS thin film has strong visible absorption to e-h pairs. The photo-generated electrons are injected into the conduction band of TiO_2 and holes acquire electrons from $\mathbf{I^-/I^{3-}}$ redox system. Application of potential make electrons flow into the external circuit, thereby registering external current as soon as the magnitude of applied potential reaches the threshold value. The bare TiO_2 electrode exhibits only negligible current as th number density of photogenrated electrons is very small due to high energy bandgap of TiO2. Energy bandgap of TiO2 lies in the UV range and energy bandgap of CdS nanoparticles lies in visible or IR range depending upon the size of nano-particle.

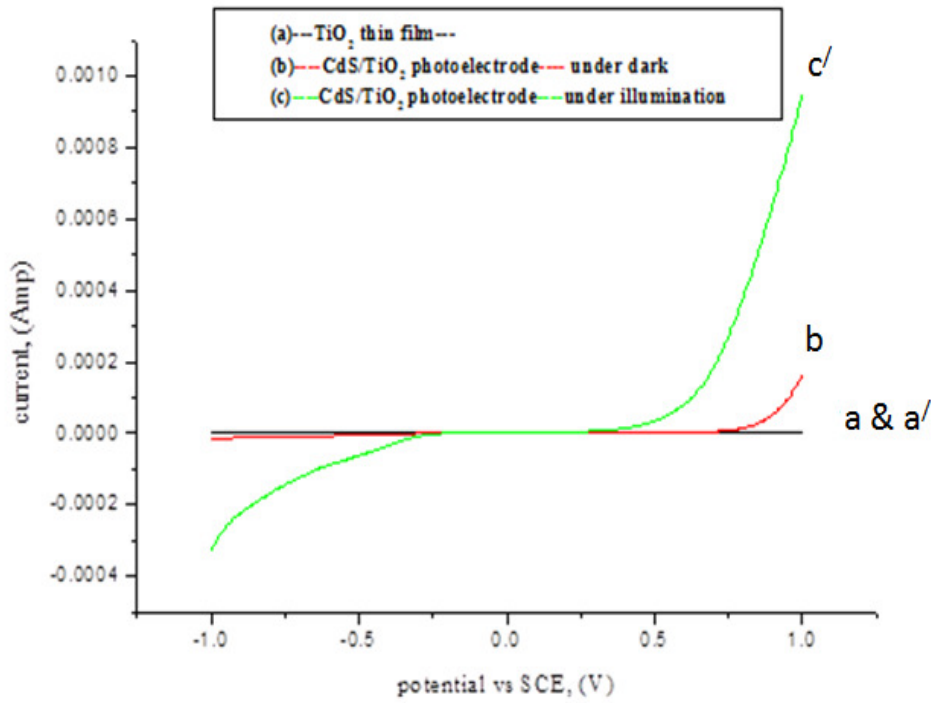

Fig.3: cyclic voltamogram of a) TiO_2 film coated substrate without illumination, a/) TiO_2 film coated substrate under illumination, b) TiO_2 film & CdS nanoparticle coated substrate without illumination and b/) TiO_2 film & CdS nanoparticle coated substrate under illumination.

4. CONCLUSION:

The present studies explore a novel and simple electrochemical approach for preparing nanostructured CdS thin film over TiO_2 thin film matrix deposited on conducting glass substrate. XRD and SEM experimental studies does confirm nanostructured growth pattern of CdS over TiO_2 matrix. PEC studies also confirming the photosensitization of TiO_2 electrode in visible region by nanostructured thin film. However further detail experimental study is still needed for better PEC performance TiO_2/CdS photoelectrode.

5. ACKNOWLEDGEMENTS

Authors are thankful Director, National Physical Laboratory, New Delhi, India for his encouragement and positive view for this research work. Dr. Sameer S. D. Mishra (senior research associate) and Mohan Pal (SRF) are thankful to Council of Scientific and Industrial Research (CSIR), New Delhi, India for providing financial assistance.

REFERENCES

[1] C. R. A. Catlow, Z. X. Guo, M. Miskufova, S. A. Shevlin, A. G. H. Smith, A. A. Sokol, A. Walsh, D. J. Wilson, S. M. Woodley, *Phil. Trans. R. Soc. A*, 368, **(2010),** 3379.

[2] K. Rajeshwar; *The Electrochem. Soc. (INTERFACE*), 6, **(1997),** 25.

[3] G. Gratzel, Insight review articles: photoelectrochemical cells, *Nature*, 412, **(2001),** 338.

[4] J. C. Colmenares, R. Luque, J. M. Campelo, F. Colmenares, Z. Karpiñski, A. A. Romero, *Materials*, 2, **(2009),** 2228.

[5] B-R Hyun, Yu-Wu. Zhong, A. C. Bartnik, L. Sun, H. D. Abrun, F. W. Wise, J. D. Goodreau, J. R. Matthews, T. M. Leslie, N. F. Borrelli, *ACS Nano*, 2, **(2008),** 2206.

[6] D. V. Talapin, J-S Lee, M. V. Kovalenko, E. V. Shevchenko, *Chem. Rev.*, 110, **(2010),** 389.

[7] B. L. Abrams and J. P. Wilcoxon, *Critical Reviews in Solid State and Materials Sciences*, 30, **(2005)**, 153.

[8] A. Shanaghi, A. R. Sabour, T. Shahrabi, and M. Aliofkhazraee, *Protection of Metals and Physical Chemistry of Surfaces*, 45, **(2009)**, 305.

[9] M. Grätzel, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 4, **(2003)**, 145.

[10] Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide and L. Han, *Japanese Journal of Applied Physics*, 45**, (2006)**, L638.

[11] H. Choi, C. Nahm, J. Kim, C. Kim, S. Kang, T. Hwang, B.Park, *Current Applied Physics* 13 **(2013)** S2-S13.

[12] H. K. Song, J. S. Yoon, J. Won, H. Kim, M. S. Yeam, *J. Nanosci. Nanotechnol* **2013**, 13, 5136.

[13] C. Liu, Y. Li, Lin Wei, C. Wu, Y. Chen, L. Mei, J. Jiao, *Nanoscale Research Letters* **2014, 9**, 107.

[14] Neil P. Dasgupta, H. J. Jung, O. Trejo, Matthew T. McDowell, Aaron, Hryciw, M. Brongersma, R. Sinclair and F. B. Prinz, *Nano Lett.*, 11**, (2011)**, 934.

[15] **P. Sudhagar, J. H. Jung, S. Park, R. Sathyamoorthy, H. Ahn and Y. S. Kang**, *Electrochemi. Acta*, 55, **(2009)**, 113.

[16] L. M. Peter, K. G. Upul Wijayantha, D. J. Riley, and J. P. Waggett, J. Phys. Chem. B, **107, (2003)**, 8378.

[17] K. Tvrdy and P. V. Kamat, *J. Phys. Chem. A***,** 113**, (2009),** 3765.

[18] R. Plass, S. Pelet, J. Krueger and M. Grätzel, J. Phys. Chem. B, **106, (2002)**, 7578.

[19] Sunil dutta Sharma, K. K. Saini et al *Applied Catalysis A : General* **314 (2006)** 40-46.

[20] Sunil dutta Sharma, K. K. Saini et. al. *Applied Catalysis B : Environmental* 84 (2008) 233-240.

[21] H. Lee, H.C. Leventis, Soo-jin Moon, P. Chen, S. Lto, S.A. Haque, T. Torres, F. Nuesh, T. Geiger, S.M. Zakeeruddin, M. Gratzel and Md. K. Nazeeruddin, *Advanced Functional Materials*, 19**, (2009)**, 2735–2742.