International Journal of Engineering Science Invention
ISSN (Online): 2319 – 6734, ISSN (Print): 2319 – 6726
www.ijesi.org || PP. 47-52

A Comparative Study of Titanium Dioxide and ZnO Nanostructured Based Dye Sensitized Solar Cell

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ABSTRACT: *A comparative study of performance of the DSSCs were done using three different photo anodes namely photo anodes prepared by coating Nano TiO_2 paste on FTO (Fluorine Tin Oxide) coated conductive glass substrates, Pure ZnO nanostructures grown by Chemical Bath Deposition Technique (CBD) on FTO glass substrates and ZnO grown over TiO_2 layer on FTO glass substrates.Its working is based on adsorption of photon by dye and its transfer to TiO_2 electrodes. In all the three cells, graphite coated FTO glass substrate was used as counter electrode. In all the three DSSCs freshly prepared electrolyte was made using Potassium Iodide,Iodine and Ethylene Glycol. EosinY was used as the dye.The V-Jcharacteristics for all the three DSSCs were obtained under sunlight to evaluate its performance and to calculate the efficiency using fill factor.The crystal structure,morphology and optical characteristics were determined using XRD,SEM and UV-Vis analysis data.*

Keywords: *Chemical Bath Deposition technique, Doctor Blade technique, Dye-sensitized solar cell, FTO,TiO_2, ZnO*

I. INTRODUCTION

Alternative energy sources are the need for the hour as fossil fuels are getting exhausted rapidly. Solar energy contributes immensely as a clean renewable alternative energy resource.In 2010, 87% of global PV(photovoltaic) sales were attributed to crystalline silicon technologies.Today the non-silicon PV market is growing rapidly and its share in the global PV market is around 20% including DSSCs[1]. DSSCs (Dye Sensitized Solar Cells) are classified as third generation solar cells that convert solar light energy into electricity based on the sensitization of wide band gap semiconductors. Modern version of dye sensitized solar cell also known as Gratzel cell was originally coinvented in 1988 by Brian O'Regan and Michael Gratzel at UC Berkley [2]. DSSCs are gaining much importance because of their low cost, environment friendly, short production time andpossibility of electricity production even in low light.DSSC is emerging as an alternative to first generation silicon solar cells. Nanoparticles of TiO_2 occur in three forms. Anatase, Rutile and Brookite.The anatase phase of TiO_2 has a wider band gap of 3.2eV compared to rutile phase which has 3eV.Hence it has better photoactivity process and is suitable as photoanode for DSSC[3]. Anataseand rutile exists in tetragonal structure, while brookite structure is orthorhombic. The dye also plays an important role in DSSC performance as it is able to harvest sunlight and transfer it to electrical energy.The main characteristics of dye is that it absorbs visible light from red to blue so that it can sensitize wide gap of material [4].On using Ruthenium Polypyridil complex as dye for Zn doped TiO_2 based DSSCs a higher efficiency of 5.63% was reported [5].The ruthenium complex based dyes being expensive a low cost but an efficient one like Eosin Y is used here.The performance and efficiencies of threeDSSCs were evaluated.

II. EXPERIMENTAL STUDY

2.1Materials Used

The fabrication of DSSC was done using TiO_2 paste(Titanium Dioxide, 2,4 Pantanedione),Arbor Scientific Company, USA, Zinc nitrate hexahydrate(Zn $(NO_3)_2.6H_2O$), Hexamine($C_6H_{12}N_4$),Potassium Iodide(KI) , Iodine(I_2), Ethylene Glycol($C_2H_6O_2$),Eosin Y($C_{20}H_6BrNa_2O_5$),[MerckChemicals], Ethanol (C_2H_5OH),deionized water and FTO substrates.

2.2DeviceFabrication

2.2.1Preparation of TiO_2 film(Doctor Blade technique) and counter electrode

The conductive side of the FTO is uniformly coated with Nano TiO_2 paste using a clean glass rod. The TiO_2 FTO substrate is then annealed at 350°C in a mufflefurnace.Another FTO substrate was coated with graphite and was used as the counter electrode.

2.2.2 Preparation of ZnO films

Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), Hexamine ($(CH_2)_6N_4$), Water (H_2O) (Merck make) were obtained from commercial sources as analytical reagents and used as purchased without further purification.

ZnO nanostructures were grown on to FTO glass substrates by Chemical bath deposition (CBD) technique. A solution was prepared by dissolving 2.4g of Zinc nitrate hexahydrate and 0.12g of Hexamine in 80mL of de-ionized water. This solution was stirred at room temperature for 1 hour in magnetic stirrer. The cleaned FTO substrate was left immersed vertically in this prepared solution kept in a constant temperature bath at a temperature of 80°C for 4 hours. FTO substrate was then removed from the solution and was annealed in muffle furnace at 500°C.

2.2.3 Preparation of ZnO –TiO_2 electrode

TiO_2 was coated on the FTO substrate using Doctor Blade technique .The TiO_2 is then annealed at 350 ^{0} C for one hourto obtain the TiO_2 photoelectrode. The CBD technique employed here is similar to that explained in the previous section. The deposition of thin layer of ZnOnanostructures on surface of TiO_2 photoelectrodes was done using the precursor solution prepared using Zinc nitrate hexahydrate and hexamine. The solution was heated by keeping it in a constant temperature bath maintained at 80 °C for four hours with the TiO_2 electrode dipped vertically into it. The ZnO coated TiO_2 photoelectrode is further annealed in muffle furnace for an hour at 500 ℃.

2.2.4 Preparation of electrolyte

Electrolyte was prepared using PotassiumIodide (KI) and Iodine (I_2).About 0.127 grams of Iodine is dissolved in 10mL of Ethylene Glycol. The above solution is added with 0.83 grams of Potassium Iodide .The solution containing Potassium Iodide and Iodine is stirred at room temperature for 30 minutes in a magnetic stirrer.

2.2.5 DyeApplication

Dye Sensitizer is the most important component in DSSC because it attracts sunlight and produces photo excited electrons.Eosin Y ($C_{20}H_6BrNa_2O_5$) of MerckChemicals was used as dye here. To prepare the dye solution 0.014grams of Eosin Y was added in 20mL of ethanol and stirred using magnetic stirrer for 30 minutes at room temperature.

2.2.6 Working Mechanism of DSSC

The Nanocrystalline TiO_2 is coated on the photo anode so as to provide large surface area to adsorb dye molecules. Upon absorption of photons, the photosensitizers are excited from the ground state (S) to the excited state (S∗). The excited electrons are injected into the conduction band of the TiO_2 electrode. This results in the oxidation of the photosensitizer (S^+).

$S + h\nu \rightarrow S*$(1)

$S* + TiO_2 \rightarrow S^+ + e-$ (2)

The injected electrons in the conduction band of TiO_2/ ZnO-$TiO_2$are transported between TiO_2/ZnO nanoparticles with diffusion toward the back contact (TCO- FTO). And the electrons finally reach the counter electrode through the circuit.The injected electron is transported between the TiO_2 nanoparticles and then extracted to a load where the work done is delivered as electrical energy. Electrolytes containing Iodine ions is used as the electron mediator between the TiO_2 / ZnO photoanode and graphite counter electrode. The oxidized molecules are regenerated by receiving electrons from theI^-ion redox mediator that get oxidized to I^-_3.TheI_3^- substitutes the internally donated electron with that from the external load and reduced back to I^-ion. The movement of electrons in the conduction band of the wide bandgap nanostructured semiconductor is accompanied by the diffusion of charge –comping cations in the electrolyte layer close to the nanoparticle surface. Therefore, generation of electric power in DSSC causes no permanent chemical change or transformation [Gratzel 2005].

2.2.7DSSC Characterization

The crystal orientation of nanoparticles was recorded by XRD (SEIFERT-JSO-2002 X-ray diffraction system- with CuKα radiation of wavelength 1.5406 Å). The morphologies of the photoanode were studied using SEM analysis (FEI Quanta FEG 200-High Resolution Scanning Electron Microscope (SEM)). It has a resolution of 1.2 nm gold particle separation on a carbon substrate. The magnification is from a minimum of 12x to greater than 100000x.Optical characteristics were determined by UV-Vis spectra.UV-vis (Analytic Jena Specord - 210plus) spectra were acquired in absorption mode. The performance and efficiency of the fabricated DSSCswereevaluated fromcurrent density-voltage (J-V) characteristics obtained under direct sunlight.

III. RESULTS AND DISCUSSION

3.1 Crystal Structure -XRD

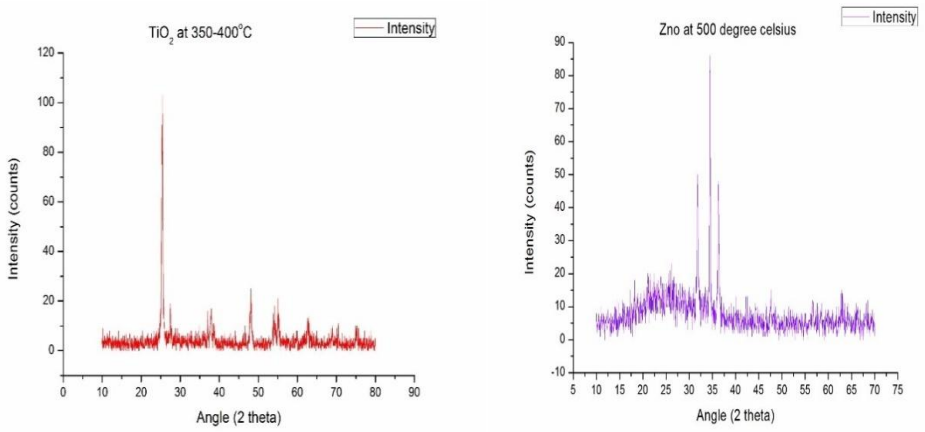

Fig.1 (a) XRD of TiO_2coating annealed at 350°C **Fig.1 (b)** XRD of ZnO coating annealed at 500°C

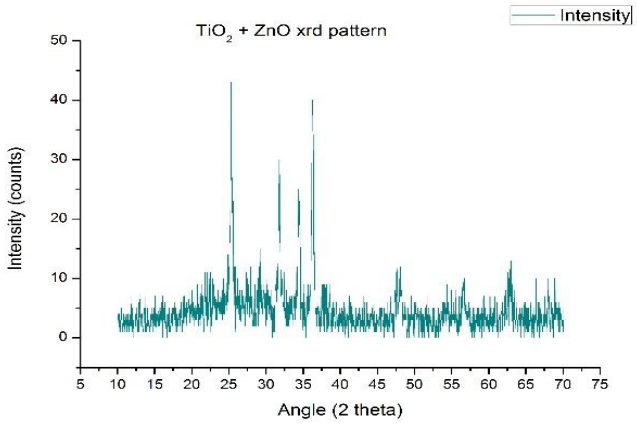

Fig.1(c) XRD image of TiO_2- ZnO films.

Fig.1a shows the XRD of TiO_2 coated on FTO using Doctor Blade Technique, annealed at 350°C.The X-ray Diffraction (XRD) analysis data was used to obtain thestructure and phase composition. Particle size can be calculated using Scherer formula using the XRD data. The experimental XRD pattern agrees with the JCPDS card no. 21-12(Anatase TiO_2) .The 2θ at peak 25.4° confirms the TiO_2 anatase phase. Strong diffraction peaks at 25° and 48° further indicated that the $TiO_2$is in the anatase phase [6]. There is no spurious diffraction peak found in the sample.The intensity of XRD peaks of the sample reflects that the formed nanoparticles are crystalline and broad diffraction peaks indicate very small size crystallite [7].Fig.1b shows the XRD analysis data of ZnO annealed at 500°C.The diffraction pattern shows a high intensity peak corresponding to the (002) plane of wurtzite ZnO whereas the peaks corresponding to other planesremained low.This shows the Nano rod growth perpendicular to the substrate. The XRD pattern of TiO_2-ZnO substrate (Fig.1c) showed the peak of anatase and rutile titania along with typical ZnO peaks at 2Θ=31.9° and 56.9°. The average grain size of all the samples were estimated from X-ray diffraction analysis by Scherer's formula [8]

$$D = \frac{k\lambda}{\beta cos\theta} (1)$$

Where$k$ represents a Scherer's factor, λ is the X-ray wavelength, β is the value of the FWHM and θ is the Bragg's angle. The grain sizes forTiO_2nanoparticles were found to be 22.24nm and for ZnO Nano particle it is found to be 21.5nm.

3.2 Surface Morphology Studies-SEM Analysis

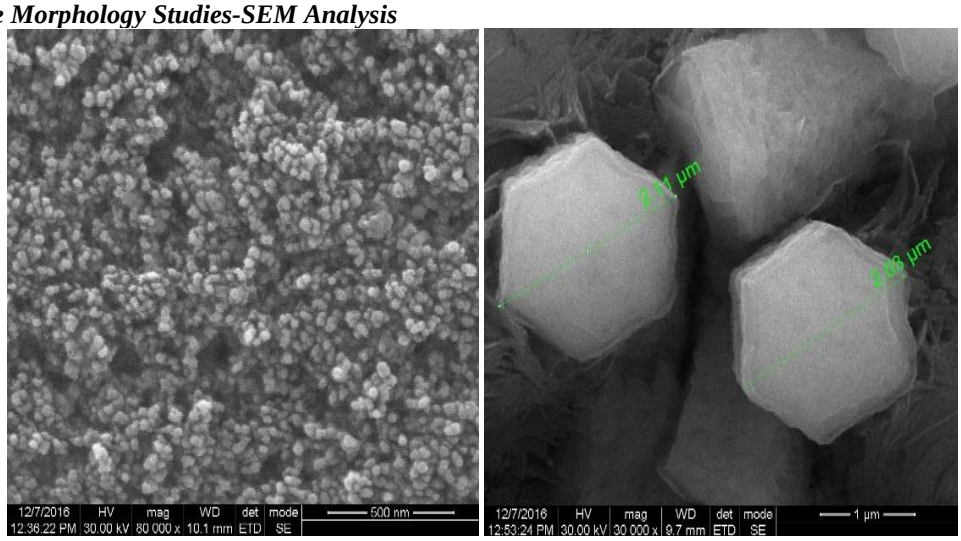

Fig.2(a) SEM image of TiO_2 **Fig.2(b)**SEM image of ZnO

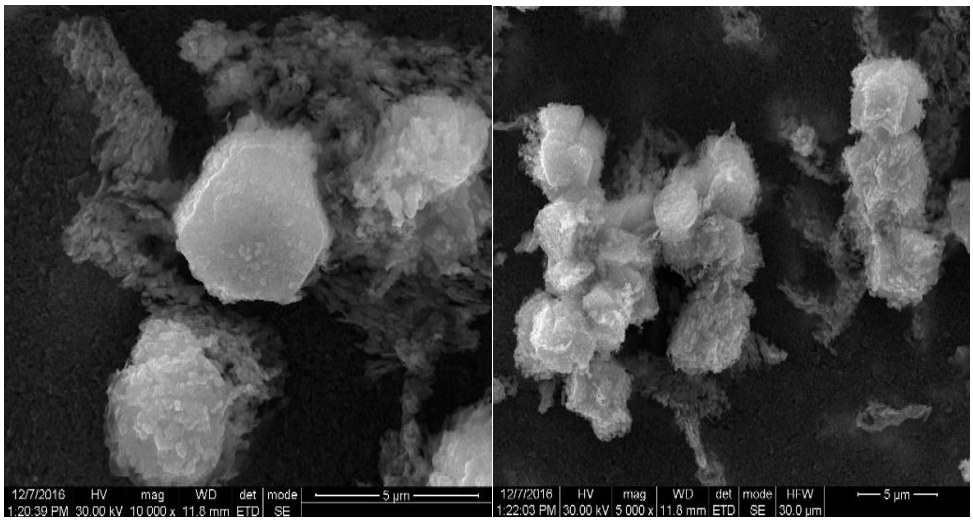

Fig.2(c) SEM image of TiO_2– ZnO film **Fig.2 (d)** SEM image of TiO_2- ZnO film

The SEM images of TiO_2 nanostructure show uniform sized spherical particle(Fig.2a) whereas the SEM images of ZnOcoatingreveal rod growth perpendicular to the plane of the substrate and hexagonal in shape(Fig.2b). In the case of TiO_2-ZnO coating, clustered nanostructures around the grown hexagonal rods were found. (Fig.2d).

3.3 Optical studies- UV-Visible Spectroscopy Analysis

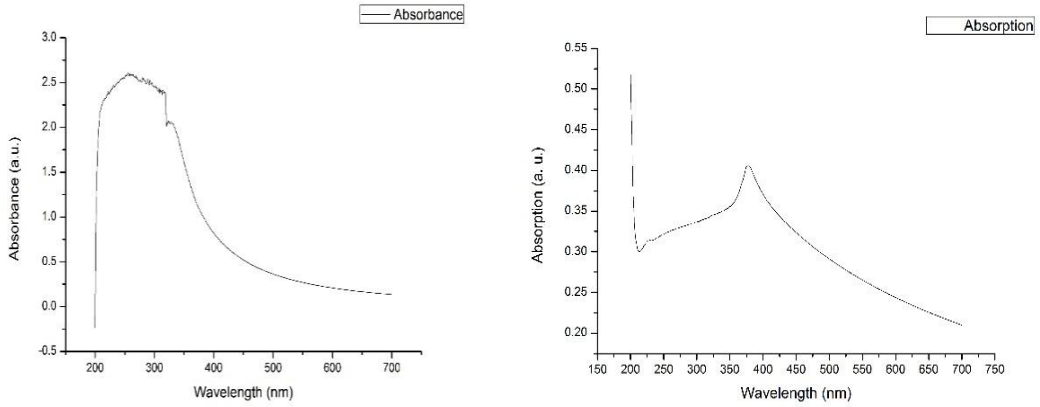

Fig.3 (a) UV-Vis Absorption for TiO_2 **Fig.3 (b)** UV-Vis Absorption for ZnO

Fig.3 (a) and Fig.3 (b) shows the absorbance spectra of TiO_2 and ZnO film. The UV-Visible absorption spectra for TiO_2 shows a broad peak over a range of 250-350 nm range of wavelength. We can infer from Figure.4b that ZnO sample absorbs maximum radiation in the UV range from 200- 420nm.

3.4 J-V Characteristics

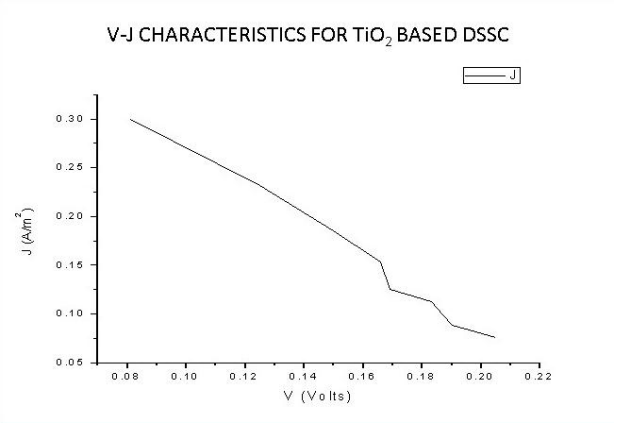

Fig. 4(a) J-V characteristics of TiO_2

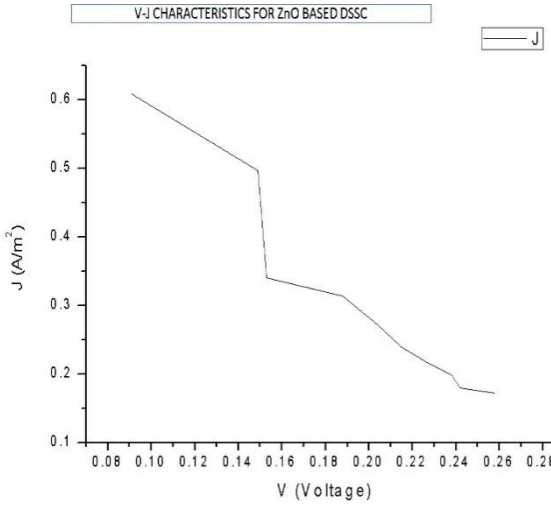

Fig.4(b) J-V characteristics of ZnO

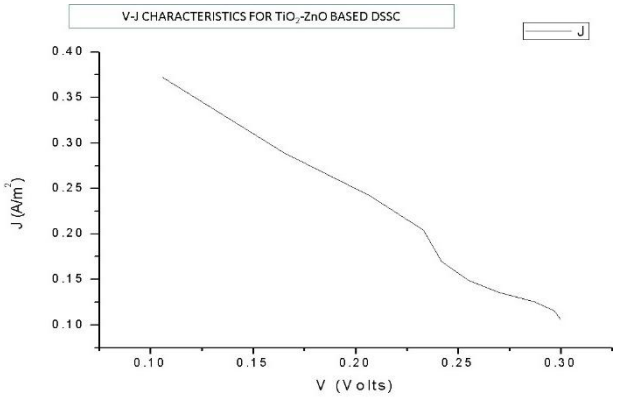

Fig.4(c) J-V characteristics of TiO_2-ZnO

The Jmax of ZnO is found to be more compared to that of TiO_2 andTiO_2 –ZnO based DSSCs.This increase in J values can be attributed to nanostructure growth pattern of ZnO photo anode.The ZnO Nanorod arrays serve as direct pathways for fast electron transport, and the ZnO nanoparticles filled in the interstitial space of ZnO Nanorods offer a large surface area for dye adsorption[9]. Using this hybrid Nano rod nanoparticle structure, a significant improvement in performance has been achieved in spite of low coated area ($1.5cm^2$) in

area. The open source V values for TiO_2,ZnO,TiO_2-ZnO based DSSCs are .205, 252 and .3V respectively.The fill factor is found to be the same for all the three DSSCs.It is also evident from the table that the efficiency calculated for TiO_2-ZnO based DSSCs are more compared to the efficiencies of other two DSSCs.The efficiency enhancement upon ZnO coating is due to the formation of an energy barrier which limits the rate of electron back recombination without affecting the dye adsorption efficiency of the TiO_2 film. This will enhance the efficiency of TiO_2-ZnO based DSSC.

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$$FF = \frac{Jmax \times Vmax}{Jsc \times Voc} \quad (2)$$

Efficiency is found using the formula,

$$\eta = \frac{Voc \times Jsc \times FF}{Pin} \quad (3)$$

Vmax, J max are the voltage and current values at maximum power point.$P_{in}$is the power input from sunlight measured using Lux meter, J_{sc} is the short circuit current and V_{oc} the open source voltage.

Photo anode Material	Area of the photo anode	V_{0C} (V)	V_{max} (V)	η (%)
TiO_2	$2.7cm^2$	0.205	0.1180	1.11%
ZnO	$1.5cm^2$	0.252	0.1099	0.868%
TiO_2-ZnO	$2.85cm^2$	0.3	0.139	1.73%

IV. CONCLUSION

Three DSSCs with TiO_2,ZnO and TiO_2-ZnO as photo anodes has been successively constructed. The J-V characteristics plotted was used to find the efficiencies.The characterization techniques adopted confirmed the anatase phase of TiO_2 and wurtzite form of ZnO. The present study of TiO_2 –ZnO double layered photo anode based DSSC prepared by simple cost effective Doctor blade and CBD technique was found to be more efficient compared to TiO_2 or ZnO based DSSCs separately.TiO_2-ZnO based DSSCs reported an efficiency of 1.73%. The efficiency enhancement is due to the formation of an energy barrier which restricts the electron back recombination.

ACKNOWLEDGEMENTS

The authors like to acknowledge the technical support of Research Laboratory, Department of Nuclear PhysicsSchool of Physical Science,Madras University;IIT SAIF, Madras; Material Science Research Lab, Department of Physics .Madras Christian College.

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