Characterization of Spin Coated TiO_2 Nanocrystalline Thin Films Via Sol-Gel Method For Fabricating Dye-Sensitized Solar Cells

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***Abstract*— Anatase TiO_2 thin films were successfully coated on Indium tin oxide (ITO) substrates using an aqueous sol of titanium (IV) butoxide. The prepared films were investigated for its structural and optical properties. X-ray diffractometer and Scanning electron microscope were used to study the structure of prepared thin films while the optical properties were investigated by recording UV – Visible spectra. Photovoltaic characteristics of the dye sensitized solar cell fabricated using the spin coated TiO_2 thin films was carried out by electrochemical impedance spectroscopy (EIS) and the efficiency of the solar cell was measured as 1.6%**

Keywords*— TiO_2, Sol-gel, spin coating, DSSC, efficiency

I. INTRODUCTION

Titanium dioxide (TiO_2) is a large band gap material with attractive electrical and optical properties, owing to which it has found a number of application in various areas. Titanium dioxide exists in three different phases, Anatase, Rutile and Brookite, of which anatase and rutile are known to be potentially active phases for many applications, such as in photocatalysis, water splitting, dye sensitized solar cells (DSSCs), sensors, paints etc. The sol-gel method is generally recognized as one of the versatile techniques for the fabrication of oxide thin films because it possesses several advantages, namely low temperature processing, ease of coating on large area, and being suitable for preparation of porous films. Dye-sensitized mesoporous nanocrystalline TiO_2 solar cells (DSSCs; also known as Gra¨tzel cells) have conventional significant attention as a potential, cost-effective alternative to silicon solar cells. DSSCs feature dye molecules chemisorbed onto the surface of TiO_2 nanocrystals.[1] The role of the TiO_2 in DSSCs is solely to act as a good electron conducting semiconductor, harvesting the electrons injected from the dye. [2]. This paper deals with the comparison of structural, optical and electronic properties of TiO_2 thin films prepared by sol gel with doctor blade technique.

II. EXPERIMENTAL TECHNIQUE

2.1Preparation of TiO_2 sol

The precursor solution was prepared by mixing titanium tetraisopropoxide, triton x -100 and 10 ml of isopropanol. After stirring this solution for half an hour, a mixture of 1 ml HNO_3, 10 ml isopropanol, and 10 ml distilled water was added drop by drop and magnetic stirring was sustained for 4 h. In addition to that the sol was aged for 2 h.

2.2 Deposition of TiO_2 thin film

Indium tin oxide (ITO) substrates were cleaned by acetone, ethanol and double distilled water successively for 15 min each in ultrasonic bath prior to coating. ITO substrates was spin coated (HOLMARC/ HO-TH-05) by the prepared sol with the rotation speed of 3000 rpm for 30s followed by drying in air for 1 min. The process was repeated for 3-4 times so as to attain the desired thickness of the TiO_2 film. For comparison commercial TiO_2 powder was used to prepare a paste and was coated on the other ITO substrate using doctor blade technique. Then, the prepared films were dried at 100˚C for half an hour and finally annealed at 450˚C for 1 h. TiO_2 film prepared by doctor blade technique is named as DB and the film prepared by sol gel assisted spin coating method as SG.

2.3 Fabrication of solar cell devices

To complete dye adsorption, the TiO_2 photoanodes were dipped in a natural dye prepared by beetroot at room temperature for 24 h. The solar cells were fabricated by assembling the dye sensitized TiO_2 films as the working electrode and Ti-coated glass substrate as the counter electrode. Then the prepared electrolyte using glacial acetic acid (0.6 ml), KI (0.1 M) and I2 (0.05 M) was introduced into the gap between the TiO_2 working electrode and titanium counter electrode of the solar cells which was clamped firmly together using binder clips.

2.4 Characterization techniques

The structural and morphological characterization were carried out for prepared TiO_2 thin films by X-ray diffractometer with Cu Kα radiation of wavelength 1.5418 Å (Shimadzu XRD 6000) and Scanning Electron Microscope (Joel JSM6390) respectively . Optical characterization was carried out by UV-Visible spectrometer (JASCO UV Vis NIR, V-670) between 200 to 800 nm. I-V characteristics of the DSSCs were analyzed by electrochemical analyzer (CHI 6008). The photovoltaic performance parameters of DSSCs were measured using a 500W Xenon light illumination with

the light intensity of 50mW/cm^2. The chosen area of dye adsorbed TiO_2 working electrodes was 0.2 cm^2.

III RESULTS AND DISCUSSION

3.1 Structural Analysis

X-ray diffractional patterns of prepared TiO_2 thin films are shown in Figure1 a and b. XRD pattern reveals that the TiO_2 nanoparticles are crystallized in an anatase phase. No traces of additional phase are found in both the XRD patterns. The intensity of the diffractional peaks of SG film is widened and reduced indicating the smaller sized nanoparticles. The average crystallite size of the nanoparticles are calculated from the Scherrer's formula [3]. The calculated crystallite size of the DB,SG particles are 14 nm and 10 nm respectively. This reduced size of the SG film may be due to the surfactant added during the sol gel process.

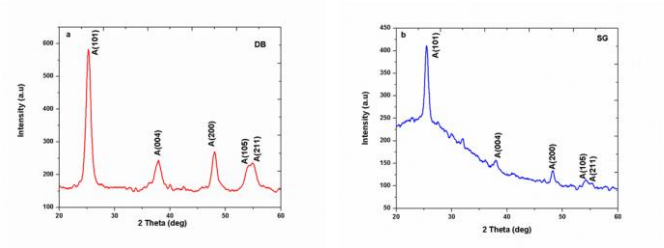

Figure 1. XRD pattern of TiO_2 thin films (a) Doctor blade method (b) sol-gel spin coated method

3.2 Morpholical Studies

Figure 2 shows the surface morphology of prepared TiO_2 films. The SEM image of DB film have more agglomerated particles leading to the high surface roughness. On the other hand, the surface of the SG film is uniform and less agglomeration of particles. It is evident from Figure 2b that the TiO_2 nanoparticles are interconnected with each other which is suitable for using TiO_2 electrode in solar cells.

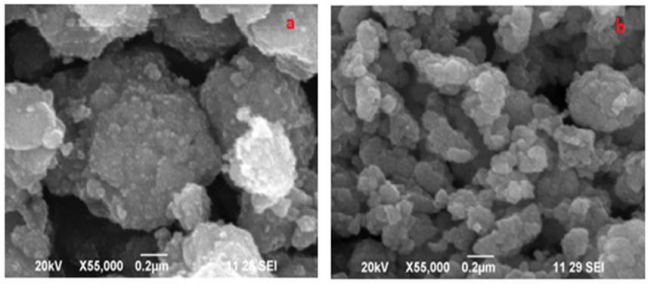

Figure 2 SEM images of TiO_2 thin films (a) Doctor blade method (b) sol-gel spin coated method

3.3 Optical studies

The optical absorption spectra of DB and SG film after dye adsorption is shown in Figure 3. The SG film shows one sharp peak at around 300nm and one small peak around 450 nm indicating higher dye adsorption which can effectively increase the effective light absorption [4]. Whereas DB film shows only one sharp peak at around 300nm. Figure 4 shows the optical absorption spectrum of prepared beetroot dye

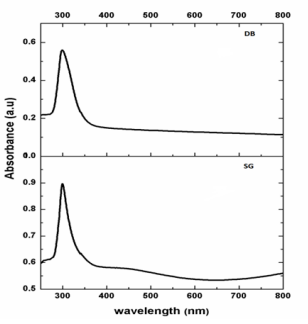

Figure 3 Absorption spectra of prepared TiO2 thin films after immersing in dye

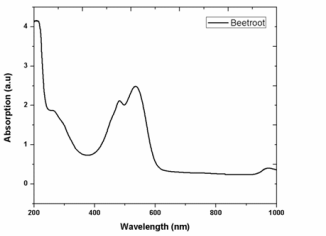

Figure 4 Absorption spectra of beetroot dye

Optical band gap energy values of the TiO_2 films were calculated using $\alpha = A(h\nu - Eg)2$ equation, where α is the absorption coefficient as a function of frequency , $h\nu$ is the energy of incident photon with frequency ν , E_g is the optical band gap energy and A is the frequency independent constant for a direct transition. By extrapolating the linear part of the curve to zero, a direct band gap of 3.29 eV and 3.4 eV were obtained for DB and SG film respectively (Figure 5). The increase in band gap energy of SG may be due to the reduced size of the particles which prepared using sol-gel assisted spin coating method [4].

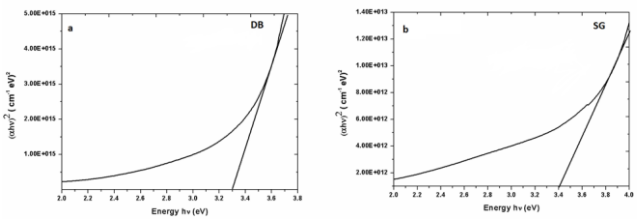

Figure 5 Band gap energy values of TiO_2 thin films (a) Doctor blade method (b) sol-gel spin coated method

3.3 Photovoltaic characteristics

Figure 6 shows the photovoltaic characteristics of fabricated DSSCs. From the J-V curve, the parameters of short circuit current density (J_{sc}) in mA/cm^2, open circuit voltage (V_{oc}) in volts, , fill factor (FF) and energy conversion efficiency (η) in % were obtained for DSSC corresponds to DB electrode are 0.45 mA/cm^2, 0.65 V, 0.56, and 0.6% respectively. While the photovoltaic parameters of the DSSC that were obtained from SG electrode are J_{sc} = 1.893 mA/cm^2, V_{oc}=0.79 V, FF=0.54 and the overall energy conversion efficiency is 1.61%. When using DB electrode in DSSC produce low photovoltaic conversion efficiency may be due to the lattice mismatch between substrate and TiO_2 nanoparticles. However when using SG electrode in DSSC the power conversion efficiency is increases. This improved efficiency is due to the enhanced necking between TiO_2 particles and between TiO_2 film and substrate resulted in more adsorption of dye and hence provided a good path for the electrons to transfer more efficiently. From the data that were obtained, the overall efficiency of DSSC is highly associated with the preparation method of TiO_2 thin film [5]. In addition, due to the layer by

layer coating during spin coating process restricts the charges to recombine at the electrolyte and ITO substrate.

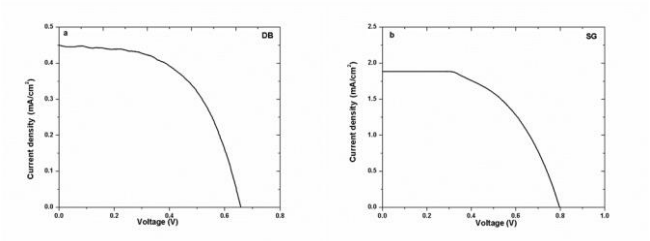

Figure 6 J-V curve of DSSCs based on TiO2 thin films (a) Doctor blade method (b) sol-gel spin coated method

IV CONCLUSION

THE PURE ANATASE TiO_2 THIN FILMS BY SOL-GEL ASSISTED SPIN COATING METHOD HAVE BEEN SYNTHESIZED. THE STRUCTURAL, OPTICAL AND ELECTRONIC PROPERTIES OF TiO_2 THIN FILMS PREPARED BY SOL GEL METHOD WERE COMPARED TO FILMS PREPARED BY DOCTOR BLADE TECHNIQUE. THE TiO_2 FILMS PREPARED BY SOL GEL METHOD HAVE BEEN IDENTIFIED TO HAVE BETTER PROPERTIES. THE SOL-GEL METHOD PROVIDES GOOD CONNECTION BETWEEN TiO_2 PARTICLES AND ALSO WITH THE SUBSTRATE, WHICH LEADS TO IMPROVED ELECTRON MOBILITY AND INCREASES THE PHOTO CONVERSION EFFICIENCY OF DSSCS.

V ACKNOWLEDGMENT

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