Mesoporous TiO_2 Thin-Film for Dye-Sensitized Solar Cell (DSSC) Application

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ABSTRACT

This paper presents the synthesis of a mesoporous thin-film of TiO_2 for its application in DSSC devices using a sol-gel method. In this, a sol-solution containing a non-ionic surfactant, Ti-alkoxide precursor, and acetic acid as a catalyst was spin-coated on conductive glass substrates. Removal of the surfactant template was accomplished by solvent leaching followed by calcination at 400-450^{o}C. The X-ray diffraction analysis of the films indicated presence of the cubic anatase phase and TEM images showed mesopores in the range of 4-8 nm. The surface roughness of the films was about 3-4 nm over an area of 600 x 600 nm^2. In another synthesis method, we are investigating deposition of TiO_2 film by infusion and selective condensation of Ti-precursor in surfactant films by the supercritical CO_2. For these films, less dye aggregation, higher surface coverage, and effective energy conversion are expected.

Keywords: Thin-film, mesoporous TiO_2, PEG-400 templating, supercritical CO_2 assisted deposition, dye-sensitized solar cell

1 INTRODUCTION

The dye-sensitized solar cell (DSSC) is a low-cost device as compared with the conventional 'p-n' junction devices and it is a potential candidate for electricity generating/conserving windows, building-integrated components, mobile telephones, military garments, consumer electronics etc. Conventional DSSC device utilizes about 5 μm thick film of TiO_2 nanocrystals to form a 'bulk' junction with a large surface area at the semiconductor/electrolyte interface that provides sufficient anchoring sites for dye sensitizers to yield effective energy conversion. The DSSC currently reaches over 10.4% energy conversion efficiency [1]. To further improve DSSC performance, new dyes or combination of dyes showing increased optical cross-sectional area are being considered.

Mesoporous TiO_2 used in DSSC offer great advantage as it renders efficient light harvesting by the surface adsorbed dye sensitizer. On a flat surface, a dye monolayer absorbs only a few percent of light. By interfacing mesoscopic structure with a dye, light absorption of a layer drastically improves. Though this improvement is significant, a critical analysis of mesoscopic structures of the TiO_2 films reported by several researchers [2-11] led to the notion that the films used so far were non-uniform with randomized pore distribution and with the less conformal surfaces [1]. Such a mesoporous film is not an ideal substrate for depositing a dye layer as it may potentially randomized orientation of the dye molecules and affect the electron transport. An ordered mesoporous continuous film structure is, therefore, strongly recommended to achieve higher efficiencies.

Mesoscopic nanocrystalline TiO_2 is synthesized by sol-gel [2], aerogel [10], and hydrothermal synthesis [4] methods. However, the information available on preparing porous TiO_2 using sol-gel derived surfactant templating method is meager. In this method, surfactant micelles self-assemble in a solution and produce a template with a uniform micelles distribution. When Ti -precursor is introduced in a solution it goes around the micelles template. Removal of the template leaves behind the imprint of TiO_2 network with the pores in place of micelles. Therefore by this method, ordered pore distribution and uniform pore size is easily achieved. In one of the recent research efforts [12], a non-ionic surfactant was used during sol-gel synthesis of TiO_2. The authors [12] reported highly porous and hydrophilic film with four times higher photocatalytic activity as compared with the TiO_2 synthesized without the use of a surfactant. Therefore, it is anticipated that the DSSC devices utilizing mesoporous TiO_2 should improve surface coverage, reduce the dye-aggregation tendency thereby effectively improving the energy conversion.

This paper reports synthesis of mesoporous thin-film of TiO_2 using PEG-400 surfactant templating approach. In another approach, synthesis of TiO_2 thin-film was attempted to prepare by infusion and selective condensation of Ti-precursor in PEG-400 surfactant film supported on a conducting electrode by the supercritical CO_2. A thorough microstructural characterization of TiO_2 films provides evidence of mesoporous phase formation. Finally, this film was employed to fabricate a DSSC thin-film device by

incorporating a sensitizer dye – N719 (Ru-based) in to the mesoporous TiO_2 structure.

2 EXPERIMENTAL

2.1 Materials

Ti-butoxide precursor was obtained from Sigma Aldrich. Polyethylene glycol (PEG)-400 surfactant was received from BASF. After dissolving PEG-400 surfactant (20 wt%) in ethanol, Ti-butoxide was added. Followed by this, an acid catalyst - acetic acid and water were added to achieve the gel formation. The gel time was varied between 1-15 min and it was dependent on the amount of acetic acid and water used during the synthesis.

2.2 Synthesis of mesoporous thin-film of TiO_2

A TiO_2 sol solution was prepared using Ti-butoxide precursor in ethanol/water in presence of acetic acid and PEG-400 surfactant as mentioned above. Based on the concentration ratio of the precursor to the surfactant and acetic acid/water, the gel time was varied between 1- 15 min. At about 80% of the total gel time, a sol-gel solution was spun at 5000 rpm on a chemically cleaned Si wafer. Three successive layers were applied. After deposition, the film was aged and annealed in a box-furnace at 400-450^{o}C for 3 h in air.

2.3 Fabrication of a dye-sensitized solar cell

In this, Indium-Tin Oxide (ITO) electrode layer was spin-coated on a cleaned glass substrate and a mesoporous TiO_2 film was deposited using a sol-gel method followed by spin coating as per the procedure outlined in Section 2.2. After TiO_2 film was annealed, a sensitizer dye - N719 dye (Ruthenium 535 bis-TBA) was applied by a dip coating technique. The ITO supported TiO_2 film was coated with N719 dye and the substrate was covered with a transparent electrode. Finally, the electrodes were sealed together using an epoxy-based sealant (Amosil-4 from Solaronix). The volume between the two electrodes was filled up with LiI and I_2 in acetonitrile.

2.4 Characterization

The ITO coated glass substrates were characterized using four-point-probe set-up. Thickness of the TiO_2 layer was measured using ellipsometer. Phase formation (rutile versus anatase) and crystal structure were determined using x-ray diffraction over a 2θ of 10-70^o as well as low angle x-ray diffraction. A detail microstructural analysis of TiO_2 thin-film was performed using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The film surface roughness or the conformality of the film was analyzed using AFM. The DSSC device was mounted on a platform and exposed to AM1.5 solar simulator and finally, I-V characteristics were recorded.

3 RESULTS AND DISCUSSION

X-ray diffraction pattern of the annealed TiO_2 film prepared by PEG-400 templating using Ti-butoxide precursor is shown in Figure 1. Sharp diffraction peaks around diffraction angles of 25^o, 48^o, and 63^o confirm the formation of the anatase crystalline phase. The slight line broadening might have been caused due to the lattice strains, lattice defects, and the experimental diffraction geometry.

A low angle x-ray diffraction pattern is presented in Figure 2, which shows at least four alternating peak positions. These peaks with a 2θ position of 1.30^o, 1.72^o, 2.17^o, and 2.36^o correspond to d-spacing of 67.62 Å, 51.24 Å, 40.52 Å, and 37.4 Å, respectively. It appears that the pore structure has periodic arrangement resembling to a simple cubic geometry.

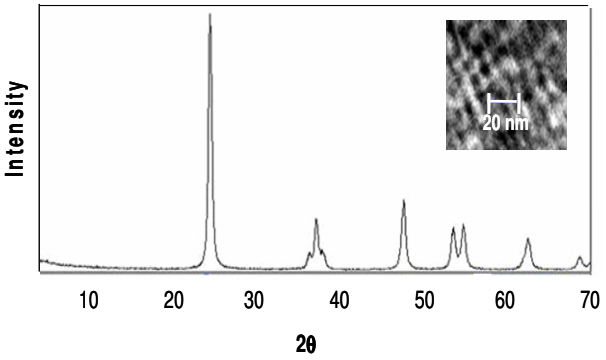

Figure 1: X-ray diffraction pattern of TiO_2 film prepared on a silicon wafer.

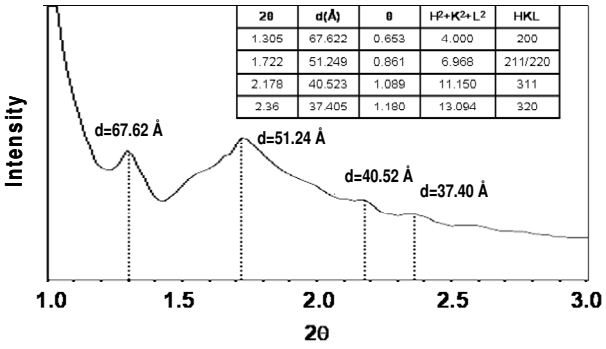

Figure 2: Low angle x-ray diffraction pattern of TiO_2 showing cubic structure of a porous film.

A TiO_2 sol-gel solution was prepared using Ti-butoxide precursor in ethanol/water in presence of acetic acid and non-ionic surfactant. Based on the concentration ratio of the precursor to the surfactant and acetic acid/water, the gel time was varied between 1- 15 min. A sol-solution was spun at 5000 rpm on a cleaned glass or Si wafer. After

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deposition, the film was aged and annealed in a box-furnace at a controlled heating rate of 0.5°C/min. The SEM image of the film deposited on Si-wafer is shown in Figure 3a exhibiting partial ordering of the mesopores. These pores were found to be in the diameter range of 2-4 nm and 7-12 nm. The surface seems to be not perfectly conformal, which might be due to the 3-layers that were deposited on the top of each other. Another film sample was found to have ordered porous and highly textured structure, which is shown in Figure 3b. The pore size was consistent with the other film sample shown in Figure 3a. This mesoporous TiO_2 film should decrease the dye aggregation tendency, increase the surface area providing more anchoring sites for dye molecules, and thus, should improve the overall performance.

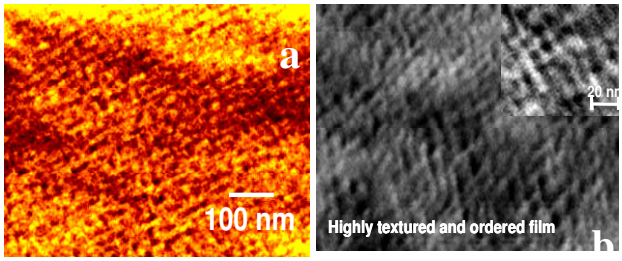

Figure 3: SEM images of the highly textured TiO_2 film film prepared by PEG-400 templaing.

Atomic force microscopic image of the TiO_2 thin-film is shown in Figure 4. This figure shows an area of 200 x 200 nm^2 and provides a representative surface structure of the film. A pore diameter of 8-12 nm was evaluated from the image. This pore size is consistent with the pore size obtained using high resolution SEM imaging technique. Additionally, as the size of the AFM probe used was 10 nm, the smaller pores could not be resolved. The surface roughness was found to be approx. 2 nm over a sample area of 200 x 200 nm^2 and it was increased to 3-4 nm over an area of 600 x 600 nm^2. Thus, highly conformal films were obtained using synthesis method provided in the Section-2.

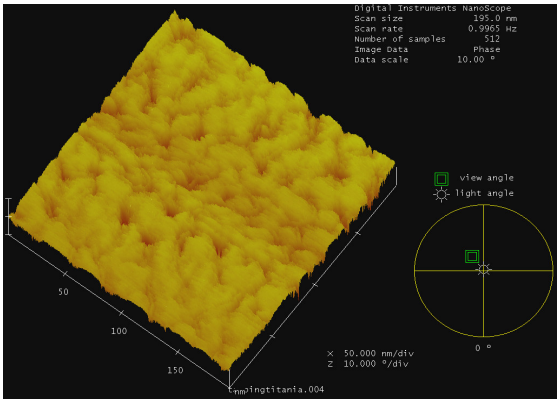

Figure 4: Atomic force microscopic image of the TiO_2 film prepared by P 123 templating showing highly conformal film with mesorporous structure.

The fabrication of a DSSC device involves integrating dye-layer coated back electrode (TiO_2 coated on ITO substrate) with ITO counter electrode separated with a non-conducting tape-like sealer. Specifically, a conducting ITO electrode layer was spin-coated on a cleaned glass substrate and a mesoporous TiO_2 film was deposited using a Ti-sol solution containing PEG-400 surfactant and an acid catalyst by spin coating. Followed by this, a sensitizer dye – N719 (Ruthenium 535 bis-TBA) was coated on the thin TiO_2 film and covered with another transparent electrode. The electrodes were sealed with an epoxy sealant and the space between the electrodes was filled-up with an electrolyte solution. The device was mounted on a platform and it was exposed to AM1.5 solar simulator and I-V characteristics were recorded. Other details can be found in Section-2.

We observed V_{oc} (open circuit voltage) of 400 mV, which is consistent with that reported by several investigators for the devices made up of P-25 based TiO_2 (thickness 5-20 μm) back electrode employing the same electrolyte [1]. Considering low uptake of a dye and having transparent back and counter electrodes, we expected poor light harvesting and thereby lower photo-induced current. One of the I-V profiles for laboratory DSSC device made with a 300 nm mesoporous TiO_2 layer coated with N719 dye is shown in Figure 5. Work is in progress to improve the light harvesting efficiency of DSSC device made with a thin-film of mesoporous TiO_2.

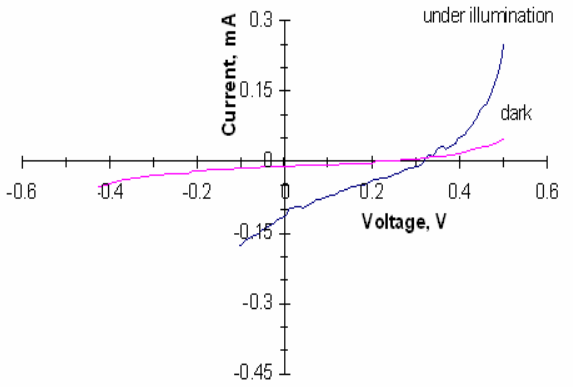

Figure 5: I-V characteristic of a thin-film DSSC device made with a 300 nm thick TiO_2 layer.

We are currently investigating the synthesis of mesoporous TiO_2 thin-film by infusion and selective condensation of Ti-precursor in surfactant films by the supercritical CO_2. For this, a cleaned glass substrate coated with PEG-400 surfactant film was loaded inside a supercritical reactor. At the reaction conditions of 60°C and 1200 psi, Ti-butoxide (diluted with ethanol) was introduced in the reactor and it was pressurized to 3000 psi with CO_2. The microstructural characterization revealed deposition of porous TiO_2 layer. Investigations are still under way to

further characterize and improve the synthesis of an ordered porous TiO_2 film using supercritical fluids.

4 CONCLUSIONS

Preliminary investigations revealed that the mesoporous TiO_2 thin-film structure is achievable using PEG-400 surfactant templating synthesis approach utilizing Ti-butoxide precursor and an acid catalyst. The film coated onto a conducting glass and processed at 400°C exhibited mainly the anatase phase with simple cubic structure. High resolution scanning electron microscopy clearly showed presence of highly textured film with a majority of pore fraction lies in the range of 7-12 nm although pores with 2-4 nm were also observed. The film with 300 nm thickness as established by the ellipsometry was found to be highly conformal as the surface roughness of the film was only 3-4 nm over an area of 600 x 600 nm^2 as analyzed using AFM. For the DSSC device fabricated utilizing the 300 nm TiO_2 film and N719 sensitizer dye, a V_{oc} of 400 mV was observed, which is consistent with that reported by several investigators for about 5 μm size film of TiO_2 nanocrystals. I-V characteristics obtained here are typical for DSSC device but it produced lower photo-induced current. One of the reasons could be that the small mesopores may not be easily accessible for the dye molecules and that will lead to poor light harvesting.

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