Morphological Studies of Mesoporous Nanostructured TiO₂ Photoelectrodes for Dye-Sensitized Solar Cells

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Abstract
Dye-Sensitized Solar Cells (DSSCs) have been fabricated by incorporating nanostructured mesoporous anatase and rutile TiO₂ photodelectrodes grown by a simple modification in hydrothermal technique. Morphological studies have been made by using Scanning Electron Microscopy (SEM). Performance investigations of anatase and rutile based DSSCs have been made by obtaining current density-voltage curve and Incident Photon to current Conversion Efficiency (IPCE) spectra. It was found that mesoporous anatase based nano DSSC has a higher efficiency (6.6%) than mesoporous rutile based nano DSSC (4.8%).

Keywords
Mesoporous, Anatase, Rutile, Solar Cells, SEM, DSSC, IPCE

I. Introduction
Dye-Sensitized Solar Cells (DSSCs) have been widely appreciated as one of the most promising several alternatives to challenge the existing conventional silicon solar cells over the past decade because of its nominal cost to performance ratio [1-4]. The main components of DSSCs are an n-type semiconductor film deposited on transparent conducting glass, a sensitizer (dye), a redox couple electrolyte and a catalyst film spread over transparent conducting glass. The sensitizing dye is chemically anchored to semiconductor surface by a carboxyl functional group. In the working mechanism, sensitizing dye molecule absorbs sunlight and generates photoexcited electron in the HOMO level of the dye. This electron gets injected into the conduction band of the semiconductor which is lying just above the HOMO level of the dye. This electron oozes through TiO₂ film to generate photocurrent. The oxidized dye regenerates itself with the help of redox couple electrolyte at dye/electrolyte interface. The injected electrons finally reach at counter electrode through external circuit. The injected electrons finally reach at counter electrode through external circuit where they reduce the redox couple which was oxidized in the dye recovery process. Thus, overall efficiency of DSSC is influenced by many factors viz. the capacity of dye to help a rapid electron generation and a fast regeneration [5-6], quick diffusion and recovery of the electrolyte [7-8], a swift electron transport in the semiconductor layer [9-10].

TiO₂ is an extensively used n-type wide band gap semiconductor with a band gap of 3.2eV [11]. TiO₂ nanocrystalline film plays a very crucial role in DSSC because of its spectacular chemical and physical properties results from nanostructures [12-14]. Usually, TiO₂ nanocrystalline films have high surface area favorable for a good deal of dye loading, high transparency and scatter negligible light because of small particle size which leads to poor light harvesting [15]. One technique to improve light harvesting capability of TiO₂ films without relinquishing accessible dye loading surface is to use mesoporous structures. Such mesoporous TiO₂ nanocrystals are supposed to simultaneously raise the light scattering as well as dye adsorption, thereby cause an increase in overall efficiency of the solar cell.

II. Experimental Methods
20mL of Titanium Tetra Isopropoxide (TTIP) was taken in a flask and 120mL of 0.1M HNO₃ was added drop wise under vigorous stirring for half an hour. Stir the solution at 80°C for 10 hours. Then the solution was divided in two parts. One flask was put in microwave at 180°C for 5 minutes and in other flask solution, 1.25mL of isopropanol was mixed and stirred the solution for 30 minutes at room temperature and then kept at 150°C for 6 hours. Afterwards, 14.8% Poly Ethylene Glycol (PEG) was added in both the solutions and stirred for homogeneous mixing. The sol was stirred until it reached at room temperature before coating and then deposited on Indium Tin Oxide (ITO) coated glass plates using dip coater (MTI Corporation) at a dipping rate of 8cm/min kept there for 10 minutes and removed at the same rate and dried at 125°C for 1 hour. Finally, one film was calcinized at 250°C and other at 550°C.

To fabricate dye-sensitized solar cells, the deposited films were kept immersed in N719 dye solution overnight. 0.5M lithium iodide (LiI), 0.05M iodine (I₂) in acetonitrile solution was used as electrolyte. Nanocrystalline structure was confirmed by x-ray diffraction (XRD) analysis. Investigations of surface properties have been made with the help of Scanning Electron Microscopy (SEM). Porosellipsometry was used to calculate the porosity values of the synthesized films. Solar cell characterizations were performed by using Keithley unit (2400 source meter). A Newport AM1.5 solar simulator (91160 A) equipped with xenon arc lamp was employed as source meter. Light intensity of the source meter was calibrated to 100 mW/cm².

III. Results and Discussions
The XRD plots for nanocrystalline anatase and rutile films are shown in fig. 1. In each spectrum shown in fig. 1, each diffraction peak corresponds to a unique crystalline phase. Nanocrystalline anatase film contains 101, 004, 112, 002, 105, 211, 204, 116 planes and 110, 101, 111, 211, 002 are the planes possessed by nanocrystalline rutile thin film. Particle sizes for the films are 26 nm and 18 nm for anatase and rutile films respectively as calculated by scherrer’s formula.
Morphological statuses of the films have been presented in SEM images (Fig. 2). The rough and porous structures are clearly visible in the images. SEM images verify the results obtained by poroellipsometry i.e. porosity of anatase film is higher (40.4) than that of rutile one (35.8).

Fig. 3: JV characteristics of dye-sensitized solar cells based on mesoporous anatase and rutile films. The Open-Circuit Voltages ($V_{oc}$) for anatase and rutile based cells are 0.73 and 0.72 respectively which are very close. But the short-circuit current density ($I_{sc}$) of anatase based cell (14.05 mA/cm$^2$) is about 30% more than that of rutile based cell (10.64 mA/cm$^2$). The overall efficiencies of the anatase and rutile based solar cells are 6.6% and 4.8% respectively.

The results of fig. 3 are in very well agreement with the absorption spectra of anatase and rutile films with dye adsorbed on these (Fig. 4).

It is clear that both the dye covered films show absorption in UV and visible range of electromagnetic spectra and rutile film absorbs lesser radiation than anatase film. The amount of radiation absorbed by dye is a decisive factor in regards to the IPCE value. Fig. 5, presents a comparative study of anatase and rutile based dye-sensitized solar cells at one sun light intensity.
The obtained parameters are again validated by diffusion coefficient (Dn) calculated by intensity modulated photocurrent spectroscopy (IMPS) using the relation [16]:

\[ D_n = \frac{d^2}{4\tau_{IMPS}} \]

where \( d \) is the thickness of the thin film and \( \tau \) indicates the relaxation time of the electrons.

Fig. 6, represents the variation in diffusion coefficient of the films with short-circuit current density and it is clear from the plots, at same value of \( J_{SC} \), diffusion coefficient of rutile film is lesser than that of anatase film. And a lesser diffusion coefficient means slower electron transport in rutile layer, thereby leading to smaller value of efficiency.

IV. Conclusion

Pure phase nanocrystalline mesoporous anatase and rutile films have been synthesized by modifies sol-gel hydrothermal process. The investigations of photon-to-current conversion efficiencies of the dye-sensitized solar cells designed by using these films have been made and a comparison of their performances has been drawn. It was found that nanocrystalline mesoporous anatase DSSC has a higher efficiency (6.6%) than that of rutile based cell (4.8%). The acquired results have been validated by absorption spectra and diffusion coefficient measurements.

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References


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