Synopsis of the proposed Ph.D. thesis

On

Theoretical and experimental studies of titanium dioxide based dye-sensitized solar cells

By

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The rising price of fossil fuels, together with their rapid depletion and the pollution caused by their combustion, is forcing mankind to find sources of clean renewable energy. Fortunately, the supply of energy from the sun to the earth is gigantic, i.e., $3 \times 10^{24}$ joule a year or about ten thousand times more than what mankind consumes currently. This means that only 0.1% of the earth’s surface with solar cells with an efficiency of 10% would suffice to satisfy our current needs [1, 2]. Therefore, solar power is considered to be one of the best sustainable energies for future generations. There are already a number of terrestrial applications where photovoltaic devices provide a viable means of power generation. Photovoltaic devices are based on the concept of charge separation at an interface of two materials of different conduction mechanism. Till date photovoltaics has been dominated by solid-state junction devices, usually based on silicon, crystalline or amorphous, and profiting from the experience and material availability resulting from the semiconductor industry. However, the expensive and energy-intensive high-temperature and high-vacuum processes are needed for the silicon based solar cells. Therefore, the dominance of the photovoltaic field by such kind of inorganic solid-state junction devices is now being challenged by the emergence of a third generation of solar cell based on interpenetrating network structures, such as dye-sensitized solar cells (DSSCs) [2, 3].

DSSCs have been extensively investigated since O’Regan and Grätzel reported a 7.1% solar energy conversion efficiency in 1991 [3]. DSSCs offer particular promise as an efficient, low cost alternative to Si semiconductor photovoltaic devices and represent a specific type of photo-electrochemical cell. The advantages of DSSCs are that they do not rely on expensive or energy-intensive processing methods and can be printed on flexible substrates using roll-to-roll methods. Instead of using a single crystal semiconductor, DSSCs rely on a thin mesoporous film (10-15 µm thick) of nano-crystals of a metal oxide, most often TiO$_2$, which is sensitized to visible light with a molecular light absorber. The sensitized nanoparticles are combined with a redox active electrolyte solution and counter electrode to produce a regenerative photo-electrochemical cell. By using the traditional liquid electrolyte, the DSSC has achieved an 11.5% efficiency record [4], encouraging the surge to explore new organic materials for the conversion of solar to electric power.
Usually the dye molecules have a low absorption coefficient. The low absorption coefficient of a dye monolayer is compensated by the mesoporous structure of the TiO$_2$ film, which leads to a strong increase in the number of TiO$_2$/dye/electrolyte interfaces through which photons pass, thus increasing the absorption probability. This phenomenon uses the increased surface area due to the associated porosity of the TiO$_2$ layer. When DSSC is illuminated, photons are absorbed by dye molecules, which inject electrons from their excited states in the conduction band of the TiO$_2$ nano-particles to leave the dye molecule oxidized. Oxidized dye molecules are reduced by a redox electrolyte, which transports the positive charges by diffusion to a Pt back electrode. Efficient electron injection from excited dye to TiO$_2$ plays an important role in DSSC [5, 6]. The injected electrons flow through the porous TiO$_2$ thin film to the transparent conducting oxide (TCO), depending on the incident intensity and trapping–detrapping effect [7–10]. Subsequently, the electrons flow to the back electrode via the external circuit. The oxidized dye molecules are regenerated by redox mediators ($I^-/I_3^-$). Finally, the oxidized redox mediators ($I_3^-$) are transported to the back electrode where regeneration of redox mediators occurs for a complete DSSC operation cycle [11, 12].

The low absorption coefficient of dye molecule can further be compensated by pumping-in more light through the front electrode using localized surface plasmons (collective oscillations of the electrons in conductors) [13]. Recently, Ihara et al. [14] have shown improvement in photoelectric conversion efficiency of DSSC by localized surface plasmon on silver (Ag) nanoparticles modified with poly acrylate-based comb-shaped block copolymer. Hägglund et al. [15] have shown the possibility to improve the conversion and cost efficiencies of DSSCs by exploiting the large optical cross sections of localized nanoparticle surface plasmon resonances. However, there is hardly any report in our knowledge on the application of plasmonic effect of Ag nanoparticle in the efficiency improvement of TiO$_2$ nanorod based DSSC [16-18].

Following research activities have been done towards completion of doctoral work:

- Study the physics behind the dye-sensitized solar cells via modeling and simulation
• Synthesis and characterization of TiO$_2$ nano-particles and nano-rods based thin films for dye adsorption and electron injection/transport

• Plasmon induced modification in the incident spectrum to improve the efficiency of DSSC

Modeling and simulation is done to explore the effect of various parameters on the electrical performance of TiO$_2$ nanoparticle/nanorod based dye-sensitized solar cells. The model could be validated by simulation software TiberCAD and the experimental results available in the literature. The results show that the porosity decreases with increasing diameter of nanorod for a fixed value of inter-rod separation. The short-circuit current density can be improved by optimizing the nanorod diameter. From this study it is observed that the nanorods of diameter from 65 NM to 90 NM with porosity range from 0.43 to 0.66 would result in better performing DSSC. Further, The steady-state current–voltage curve and dynamic response of a DSSC is mathematically modeled based on the electrical equivalent circuit. The effect of temperature and illumination on the steady state and dynamic parameters of dye-sensitized solar cells are studied. It is found that the dynamic resistance of DSSC decreases from 619.21 $\Omega$ to 90.34 $\Omega$ with an increase in illumination level from 200 W/m$^2$ to 800 W/m$^2$. A positive temperature coefficient of dynamic resistance is observed. The interfacial charge transfer and recombination losses at the oxide/dye/electrolyte interface are found to be the most influential factor in the overall conversion efficiency and included in the mathematical model. The saturation current of rectifying diode and saturation current of recombination diode are responsible for the transfer recombination losses and have a major influence on the overall conversion efficiency.

Preparation and characterization of the nano-crystalline TiO$_2$ based working electrodes was done. The working electrode consists of a layer of porous TiO$_2$ material on FTO coated glass substrates. Various TiO$_2$ layer deposition methods, such as spray-pyrolysis, hydrothermal method, and doctor-blade method have been tried out. The scanning electron microscopy (SEM) is done for morphological characterization of these layers. X-ray diffraction technique is used to explore the phases of TiO$_2$ in the layer.
Surface profilometer is used to explore the exact thickness and roughness of the layer. Further, these electrodes have been used as a working electrode of DSSC and the current-voltage characterization is done to explore their actual device performance. The TiO$_2$ layers developed by a doctor-blade method has performed better than others. The fabrication of dye-sensitized solar cells with Ruthenium-based sensitizer dye as absorbers is described and the effect of electrode morphology on solar cell performance is presented. A dye-sensitized solar cell is fabricated with $\approx$12 $\mu$m thick TiO$_2$ layer, produced power conversion efficiency of 2.9% under AM1.5 spectrum with photo-generated current density of 7.2 mA/cm$^2$ and open-circuit voltage of 672 mV. An entire electrochemical phenomenon of TiO$_2$-electrolyte interface, diffusion of electrolyte and charge transfer at counter electrode is mathematically modeled using an electrical equivalent circuit. The effect of temperature and illumination on the steady state and dynamic parameters of dye-sensitized solar cells are also studied.

In order to quantify enhanced light trapping in terms of the number of photons, when light passes through the plasmonic Ag nanoparticle layer placed over FTO, a set of experiments were performed. Glass substrates coated with FTO having sheet resistance $\approx$ 10 $\Omega$/$\square$ were cleaned sequentially by ultrasonic treatment in detergent, de-ionized water, acetone and isopropyl alcohol and dried with nitrogen before film preparation. A very thin silver layer was deposited on the FTO glass substrate (TEC8, Pilkington Glass) using silver wire of purity 99.9998% (Alfa Aeser) by thermal evaporation method (base pressure $\approx$1 ($10^{-6}$ bar, BC300, HHV make). Thickness was recorded from the thickness monitor supplied with the thermal evaporation system. The deposition was followed by vacuum annealing of the samples at 250 °C for 2 hours. Optical properties of the samples were investigated by LAMBDA$^{TM}$ 750 of Perkin Elmer at CEN, IIT Bombay. The measurements were done in reflection and transmission mode. The samples were further characterized by atomic force microscopy (AFM) for topographic information.

An improvement in the photoelectric conversion efficiency of a dye-sensitized solar cell is reported by simulating DSSC with plasmon enhanced light trapping in the absorbing region observed experimentally. Improved light transmission is observed experimentally in silver nanoparticle coated FTO glass. The size of Ag nanoparticle is
estimated as 110 nm by comparing theoretical results with experimental data. The transmission data is used to explore the effect on electrical parameters of dye-sensitized solar cell using theoretical model. Plasmon enhanced DSSC showed increased efficiency of 11.76% under AM1.5 solar spectrum compared with 10.86% for a DSSC without Ag nanoparticles. Localized surface plasmon resonance incurred by Ag nanoparticles is also used to enhance the photoelectric conversion efficiency of a TiO$_2$ nanorod based dye-sensitized solar cell (DSSC). The transmission data is used to explore the effect on electrical parameters of TiO$_2$ nanorod based DSSC using theoretical model. Current density increased from 11.7 mA/cm$^2$ to 12.34 mA/cm$^2$ and the open - circuit voltage increased from 704 mV to 709.5 mV. Overall efficiency enhancement of 6.67% is shown in TiO$_2$ nanorod based DSSC due to plasmon induced light trapping.

It is proposed to divide the thesis into six chapters. A chapter-wise description of the thesis is given below:

**Chapter 1** is the introduction and literature review, in which the research activities in photovoltaics have been discussed and research problem is defined. It also highlights the contributions from the investigation.

**Chapter 2** gives the details of different experimental techniques to prepare nano-crystalline TiO$_2$ layers act as working electrode for DSSC, like spray pyrolysis, hydrothermal method and doctor blade method. It also includes a brief description of the characterization techniques such as XRD, SEM, AFM, UV-Vis-NIR spectrophotometer, Impedance spectroscopy, Capacitance-voltage measurements and Current-voltage measurements.

**Chapter 3** gives the details of modeling and simulation of nano-crystalline TiO$_2$ based DSSCs. A MATLAB/Simulink code was written based on proposed theoretical model to predict performance of DSSC.

**Chapter 4** gives the details of structure and surface morphology of TiO$_2$ layers studies by surface profilometer, XRD and SEM. It also deals with the fabrication of dye-sensitized solar cells with Ruthenium-based sensitizer dye as absorbers and the effect of electrode morphology on solar cell performance.
Chapter 5 describes the role of surface plasmons in improving light trapping. The enhanced transmission observed in Ag nano layer deposited FTO glass is used in simulation for predicting efficiency.

Chapter 6 gives the Summary of work and Conclusions drawn from the entire work along with some recommendations for future work.

LIST OF PUBLICATIONS

(A) Accepted in International Journals


   http://dx.doi.org/10.1155/2013/646407

(B) Conferences


(C) Papers not included in thesis


References:


