International Journal for Multidisciplinary Research (IJFMR)



• Email: editor@ijfmr.com

Analysis of Photovoltaic Properties of A Quasi Solid State Dye Sensitized Solar Cell Based on **Cu Pthalocyanine**

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Abstract

DSSCs are fabricated employing Cu-pthalocyanine (Tetrasulphonated) dye as photo sensitizer, polymer sol gel as electrolyte with PEDOT:PSS coated FTO as counter electrode. In order to enhance the efficiency, the effect of the TiCl₄ (Titanium Tetrachloride) post-treatment on nanocrystalline TiO₂ films in Quasi solid state dye sensitized solar cells (DSSCs) is investigated and compared to nontreated films. The performance of both TiCl₄ treated and nontreated DSSCs are analyzed by optical absorption spectra, current-voltage characteristics in dark and under illumination etc. .As a result of this post-treatment, a significant increase in conversion efficiency and short circuit current density is observed. The overall power conversion efficiency improves from 2.68 % to 3.5% upon TiCl₄ treatment. This improvement is attributed to increase in dye loading, enhancement in electron lifetime and shift in the conduction band edge upon TiCl₄ treatment. Here, the shift in the conduction band edge of the TiO₂ upon TiCl₄ treatment creates a driving force for charge transfer from the LUMO of the dye molecules to the conduction band of TiO₂ which results in improved charge injection.

Keywords: Dye sensitized solar cells (DSSCs), Dye binding sites, Titanium Tetrachloride treatment.

1. INTRODUCTION

Dye-sensitized solar cells (DSSC) provide a technically and economically credible alternative concept to present day p-n junction photovoltaic devices. In contrast to the conventional systems where the semiconductor acts as light absorbent and charge carrier transport, the two functions are separated in DSSC. Light is absorbed by a sensitizer anchored to the surface of a wide-band semiconductor. Charge separation takes place at the interface via photo-induced electron injection from the dye into the conduction band of the solid. Carriers are transported in the conduction band of the semiconductor to the charge collector. The use of broad absorption band sensitizers in conjunction with nanocrystalline oxide films permits harvesting of a large fraction of sunlight. Nearly quantitative conversion of incident photons into electric current is achieved over a large spectral range extending from the UV to the near IR region. Overall solar (standard AM1.5) to current conversion efficiencies (IPCE) over 10% have been reached and there are good prospects to produce these cells at lower cost than conventional devices. Since their breakthrough in 1991 as reported by Gratzel et.al., [1], the DSSCs have been attracting a significant attention of the researchers due to their substantial possibilities to fabricate low-cost ,environmentally friendly, large-area photovoltaic devices. These cells are composed of a wide band gap semiconductor (like TiO₂, ZnO) deposited on a transparent conducting substrate, an anchored molecular sensitizer, a



International Journal for Multidisciplinary Research (IJFMR)

E-ISSN: 2582-2160 • Website: <u>www.ijfmr.com</u> • Email: editor@ijfmr.com

redox electrolyte (I-/ I3- couple) and a counter electrode [1, 5]. DSSCs based on Ru- complex photosensitizers, such as N3, N719 and black dyes have shown high PCE [9-10]. In recent years, metal free organic dyes have been explored as an alternative to Ru-complexes because of low material costs, ease of synthesis and high molar extinction coefficients [9-12]. Although DSSCs based on metal free organic dyes as sensitizers, with considerably good efficiencies have been reported [13-14], yet there is a need to optimize their chemical and physical properties for improving device performance.

Extensive research is being carried out to optimize the factors for improving the efficiency of DSSCs, such as enhanced diffusion of dye, choice of electrodes and optimization of electrolytes etc. Extent of diffusion of dye into nano-crystalline TiO_2 matrix significantly affects efficiency and photocurrent in DSSCs. The electron transport at the dye / nanocrystalline semiconductor interface is a key step in the energy conversion process as photo excited electrons in dye molecules are transferred to an external circuit through this semiconductor film. Electron transport is sensitive to the structure of the dye since electrons passes through its overlapping molecular orbitals and semi-conductor surface. Electron transport process is also affected by how and where the dye is adsorbed over the surface.

Extent of diffusion of dye into nano-crystalline TiO_2 matrix significantly affects efficiency and photocurrent in DSSCs. There are various methods to increase the dye diffusion into TiO_2 matrix. One of such significant method is titanium tetrachloride ($TiCl_4$) post-treatment of the TiO_2 film. The TiCl4 surface treatment causes improvement in electron transport and dye anchoring, resulting in enhanced efficiency for the solar cells [15].

Herein we have investigated and compared the performance of DSSCs based on untreated and TiCl₄ treated TiO₂ electrodes. DSSCs have been fabricated using both TiCl₄ treated and untreated -nanoporous TiO₂ films as base electrodes, tetra sulphonated copper pthalocyanine (CuTsPc) dye as photo sensitizer , polymer sol gel as electrolyte and PEDOT:PSS coated FTO as counter electrode.

The performance of both TiCl₄ treated and untreated DSSCs are analyzed by optical absorption spectra, current–voltage characteristics in dark and under illumination .We observed a significant increase in incident photon to current conversion efficiency (IPCE) and short circuit current density (Jsc) upon TiCl₄ treatment as compared to untreated films. The overall power conversion efficiency improves from 2.68 % to 3.50 % upon TiCl₄ treatment. This improvement is attributed to increase in dye loading, enhancement in electron lifetime and shift in the conduction band edge upon TiCl₄ treatment. Here, the shift in the conduction band edge upon TiCl₄ treatment. Here, the shift in the conduction band edge of the TiO₂ upon TiCl₄ treatment creates a driving force for charge transfer from the LUMO of the dye molecules to the conduction band of TiO₂ which results in improved charge injection.

2. Experimental details

2.1. Preparation of photo-electrodes:

Fluorine doped tin oxide (FTO) glass plates were cleaned in detergent solution, rinsed with de-ionized water & acetone and dried in ambient conditions. A TiO2 colloidal dispersion was prepared by adding 6gm of TiO2 (P25 Degussa product) powder in 2 ml of distilled water. Further, 0.2ml of acetyl acetone (particle stabilizer) was added to prevent the re-aggregation of TiO2 particles. Finally 8.0ml of distilled water and 0.1ml of Triton X-100 (to lower the surface tension of the colloid in order to facilitate easier spreading onto the conducting glass plate) were slowly added with continuous mixing for 10 min. A plastic adhesive tape was fixed as spacer on the three sides of conducting glass substrate (FTO) to restrict the area and thickness of TiO2 film. A plastic adhesive tape was fixed as spacer on the three sides of conducting spacer on the three sides of conducting the spacer on the three sides of conducting the spacer on the three sides of conducting spacer on the three sides of conducting the spacer on the three s



glass substrate (FTO) to restrict the area and thickness of TiO2 film. The prepared colloidal paste of TiO2 was spread over FTO substrate employing Doctor blade technique to obtain a nanocrystalline layer. After the TiO2 layers get dried, the films were sintered at 450°C for 30 minutes in air to improve the electronic contact among particles and to burnout organic binders.

2.2 TiCl₄ Post Treatment:

Freshly sintered TiO2 film was treated with TiCl4 employing the method as described in literature [16-19]. For post-treatment with TiCl4, an aqueous stock solution of 2 M TiCl4 was diluted to 0.05 M. Sintered TiO2 film was immersed into this solution in an air tight closed glass vessel for 24 hours and then was taken out and dried. After TiCl4 treatment, the films were calcined at 450°C for 30 minutes.

2.3 Dye Sensitization of photo electrodes:

The sensitization of TiCl4 treated TiO2 and untreated TiO2 electrodes were carried out by overnight immersion in the solution of CuTsPc dye dissolved in DMF at 70°C. Films were washed again with the solution and were allowed to dry for 30 min.

2.4. Fabrication of dye sensitized solar cells and their Characterization:

A quasi solid state polymer electrolyte was prepared by mixing LiI (0.1 g), I2 (0.019 g), propylene carbonate (5 mL), P25 TiO2 (0.0383 g), PEO (0.2648 g), and 4-tert-butylpyridine (0.044 mL) into acetonitrile (5 mL) solvent as reported in literature. TiO2 (P25 Degussa) powder was added as nano-fillers in the polymer electrolyte. This electrolyte was then spread over the dye sensitized photo electrodes by spin coating method to form the hole transporting layer. The counter electrodes were made by developing a thin film of protonated poly-(3,4-ethylenedioxythiophene)-polystyrene (PEDOT:PSS) over graphite coated FTO glass substrates. In this process, first the FTO is coated with graphite and then DMSO treated PEDOT:PSS was grown over the top of the film by spin coating method. The counter electrode was allowed to dry at 80°C for 30 min. The DSSCs were made by clamping the photoelectrode consisting of polymer electrolyte with counter electrode.

We have fabricated quasi solid state DSSCs with following configurations:

(a) FTO / TiO2–CuTsPc / quasi solid state electrolyte / PEDOT:PSS coated FTO (device A)

(b) FTO/ TiCl4 treated TiO2 –CuTsPc /quasi solid state electrolyte /PEDOT:PSS coated FTO (device B) The current–voltage (J–V) characteristics in dark and under illumination were recorded by a Keithley electrometer with built in power supply. A 100W halogen lamp was used as light source with intensity of approximately 100mWcm-2 (as measured by Lux meter equipped with silicon detector).

3. Results and discussion

3.1 Characterization of electrodes

To understand the effect of TiCl4 treatment on the surface of TiO2 electrode and to estimate the relative increase in dye loading, we have carried out dye de-sorption experiment on untreated and treated TiO2 films as described in literature.[20] For both treated and untreated TiO2 films , dye was desorbed from the electrodes by treating with a quantified amount of diluted NH3 in water, resulting in a dye solution of which a UV /vis spectrum has been recorded. The relative difference in absorbance may be directly translated into the relative difference in dye loading of the TiO2 surface as the absorbance is linearly related to the concentration of dye. The difference in absorbance between TiCl4-treated and untreated TiO2 is distinctive, showing almost 21% higher dye loading for TiCl4-treated electrodes. It may be interpreted as TiCl4 treatment has increased porosity of the surface and this surface modification apparently increases the amount of adsorbed dye molecules.



3.2 Current–voltage characteristics:

The J–V characteristics of device A and device B, under the illumination intensity of 100 mW/cm2 are shown in Figure 1 (a). The photovoltaic parameter, i.e. short circuit current (Jsc), open circuit voltage (Voc), fill factor (FF) and power conversion efficiency (η) as estimated from these curves are compiled in Table 1. Obtained data indicates an improvement in all the photovoltaic parameters upon TiCl4 treatment. The value of overall power conversion efficiency i.e. 2.68% for device A based on untreated TiO2 electrode increases to 3.50% upon TiCl4 treatment in device B .The Jsc of DSSCs is mainly influenced by the sensitizer(dye) loading and the electron transfer efficiency in the TiO2 film. The dye loading for treated TiO2 electrode is about 21% higher than that for untreated TiO2 electrode, therefore the increase in dye loading may be considered as one of the significant factor for the increase in Jsc. TiCl4 treatment provides additional adsorption sites for the dye on TiO2 surface resulting in increased dye loading which in turn causes an increase in Jsc.



The Voc in DSSCs is directly related with the concentration of electrons injected from the LUMO of the dye to the conduction band of TiO2. The higher short circuit density could be attributed to a downward shift (towards more positive potentials on the electrochemical energy scale) of the conduction band edge in the TiO2; thus, leading to an additional driving force and optimized electron injection form the excited state of the sensitizer. However, at the same time the shift was expected to lower the VOC by reducing the distance between conduction band edge and the iodide/iodine potential. This shift was compensated by a reduced electron recombination rate; therefore, the open circuit potential was not affected negatively. The effect of TiCl4 treatment is further confirmed by the J–V characteristics in dark as shown in Fig. 1(b). The origin of dark current in DSSC is due to the porous nature of TiO2 structure, which provides pathways for liquid redox electrolyte (i.e. I3 – species) to penetrate through the porous film and contact the FTO surface. During the penetration, electron recombination takes place and causes reduction in photocurrent. It can be seen from this figure that the dark current decreases upon TiCl4 treatment(in device B) as compared to the untreated device (in Device A). The dye desorption experiments here confirms that the TiCl4-treated electrodes adsorb 21% more dye than the nontreated electrodes. This increase in dye adsorption may be attributed to availability of more specific binding sites on the TiO2 surface upon TiCl4 treatment. Thus the most obvious fact causing an increase in short circuit current and efficiency upon



TiCl4 treatment may be attributed to increased dye adsorption on TiO2 surface.

Figure 2(a) also shows that the slope for the TiCl4 treated TiO2 (0 .128) is 39.13 % higher than that for untreated TiO2 (.092) electrode. It indicates that 39.13 % more electrons are collected from the same amount of photogenerated electrons at FTO surface upon TiCl4 treatment. This confirms that TiCl4 treatment of TiO2 electrode in DSSCs facilitates electron transfer at the interface, resulting in an increase in collection efficiency.



Open circuit voltage decay (OCVD) technique has been employed as a powerful tool to study the electron lifetime in DSSC's. This technique also provides some quantitative information on the electron recombination rates in DSSCs. In order to conduct the OCVD measurement, the device is illuminated with white light and a steady state voltage is obtained. The decay of voltage is then monitored after interrupting the illumination. The measured decay of the photo voltage reflects a clear decrease in electron concentration at the FTO surface, which is mainly caused by the charge recombination. Figure 2 (b) shows the OCVD curves of DSSCs based on untreated and TiCl4 treated TiO2 electrodes. Theses curves indicates that the OCVD response of device B (TiCl4 treated TiO2) is much slower than that of device A (untreated TiO2). From the OCVD measurement, the electron lifetime (τ_n) is determined by the reciprocal of the derivatives (dVoc/dt)⁻¹ of the decay curves normalized by the thermal voltage (kT/q), using the following expression:

$$\tau_n = \left(\frac{KT}{q}\right) \left(\frac{dV_{oc}}{dt}\right)^{-1}$$

The value of τ_n for the DSSC with TiCl4 treated TiO2 film is longer than that for untreated TiO2 film. It suggests that electron injected from the excited dye can survive for a longer time upon TiCl4 treatment and hence facilitates electron transport without undergoing losses at FTO surface. Therefore, OCVD measurements demonstrate that due to the longer electron lifetime, the photoelectron recombination rate is reduced effectively upon TiCl4 treatment of TiO2.

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Device	Short circuit current (Jsc) (mAcm ⁻²)	Open circuit voltage (Voc) (V)	Fill factor	(η) (%)
Α	5.14	0.66	0.79	2.68
В	6.16	0.73	0.78	3.50

Table-1 Photovoltaic parameters of the quasi solid state dye sensitized solar cells

4. CONCLUSION:

Quasi solid state DSSCs based on TiCl4 treated and untreated nanoporous TiO2 electrodes using CuTsPc dye as photo-sensitizer and PEDOT:PSS coated FTO as counter electrode have been fabricated. The performance of the DSSCs have been investigated systematically employing J–V characteristics in dark and under illumination and OCVD measurements. It was found that the PCE significantly improves from 2.68 % to 3.50 % upon TiCl4 treatment. The improvement in the PCE is due to an increase in dye loading or availability of more specific binding sites on the TiO2 surface upon treatment. The post-treatment with TiCl4 increases the surface area of the TiO2 layer through the deposition of additional TiO2 particles on the existing nanoporous layer. Hence, a higher dye adsorption could be achieved. We have analyzed that TiCl4 treatment causes a shift in the conduction band edge of TiO2 which is an important factor responsible for observed increase in the efficiency upon TiCl4 treatment. Due to the longer electron lifetime, the photoelectron recombination rate is reduced effectively upon TiCl4 treatment of TiO2. The higher short circuit density could be attributed to a downward shift of the conduction band edge in the TiO2 ; thus, leading to an additional driving force and optimized electron injection form the excited state of the sensitizer.

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