

Solid State Photovoltaic Cell Made from Cu/n-Cu₂O/Rhodamine-C₁₈/p-CuI Thin Films and Carbon Nanotubes as Upper Electrode

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Abstract—Dye sensitized thin film solar cell was prepared by using Cu/n-Cu₂O/R-C₁₈/p-CuI layers and CNT as upper electrode. A simple method was used to prepare the Cu₂O layers by boiling the copper plates in a CuSO₄ (10⁻³M) Solution. p-CuI colloidal solution was lightly spread on the Cu/n-Cu₂O surface to fabricate the Cu/n-Cu₂O/p-CuI photoelectrode. The band gap of n-Cu₂O was ≈ 1.9eV and CuI was ≈ 3.1 eV. Dye sensitized solid state photovoltaic cell (DSSC) with Cu/n-Cu₂O/R-C₁₈/p-CuI was studied by controlling the formation of dye aggregates of R-C₁₈ Langmuir-Blodgett (LB) films on the p-CuI layer. CNT layer was performed as the upper electrode of the solar cell. In this paper the diffuse reflectance spectra, photocurrent action spectra, I-V characteristics and stability curves were used to discuss the characteristics of solid state thin film solar cell. The maximum power conversion efficiency is 2.5% for the device without CNT as upper electrode and it becomes 4% with CNT layer as the upper electrode. Photocurrent enhancement is believed to be the enhancement of light absorption of the monomeric LB dye layer and effective charge collection and separation due to CNT upper electrode.

Keywords— n-Cu₂O, Carbon nanotube (CNT), thin film solar cell

I. INTRODUCTION

Solar cells have been at the heart of current low-carbon economy and have led to growing interest in the field of environmental and energy applications because of the depletion and pollution of fossil fuels. Among various solar cells, dye-sensitized solar cell (DSSC) is a promising solution to global energy and environmental problems because of its clean, low-cost, high efficiency, good durability and easy fabrication. However, enhancing the efficiency of the DSSC still

is an important issue [1-4]. Among the dye deposition techniques Langmuir Blodgett (LB) film deposition technique has an ability to deposit dye films onto the substrate by controlling the dye aggregates and orientation of the dye on various substrates with abias voltage [3,4].

Cuprous oxide (Cu₂O) is a well-known p-type and n-type semiconductor with a direct band gap of 2.0 eV [1-3]. Cu₂O thin films have high optical transmittance at wavelengths above 600 nm with a slightly reddish black appearance and a high optical absorption coefficient at the wavelengths below. Cu₂O in thin-film form is an attractive material for many device applications because of its p-type and n-type semiconductivity, high absorption coefficient, abundant availability, non-toxic nature, and low production cost [4-5]. Cu₂O thin films find diverse applications in oxygen and humidity sensors, electrochromic devices [6] and photovoltaic devices such as thin-film hetero-junction solar cells [7-9]. Cu₂O thin films can be prepared by various techniques such as activated reactive evaporation, thermal oxidation, vacuum evaporation, chemical vapour deposition, sol-gel process, electro-deposition, sputtering and simple boiling process [10-17]. Among these deposition techniques, boiling process is one of the best techniques for preparation of n-type Cu₂O thin films due to the advantages of high deposition rates, excellent uniformity over large area substrates and good controllability [3-4].

Recently CuI was used as a hole-collecting agent in dye-sensitized solid state cells [5]. CuI has a band gap of 3 eV, so its interface with n-type copper oxides must form n-Cu₂O/p-CuI junction photovoltaic cell.

CNT transparent electrodes, which provide electrical contact to the active layer and allow light to pass through, are ubiquitously used in solar cells with increasingly large industry demands [6]. The role of interconnected CNTs in the photovoltaic research field is popular because of the potential to make novel thin film solar cells, whilst increasing the overall efficiency of the device [7-8]. In this research work, thin film solar cell was prepared by using Cu/n-Cu₂O/R-C₁₈/p-CuI layers and CNT as upper electrode.

II. EXPERIMENTAL DETAILS

D. Preparation of Cu/n-Cu₂O/Dye/p-CuI/ITO junction photoelectrode

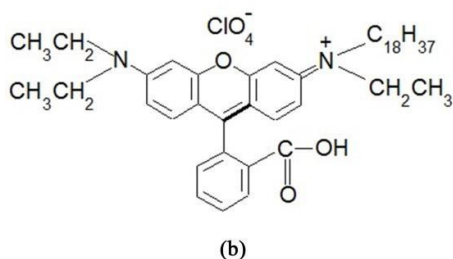
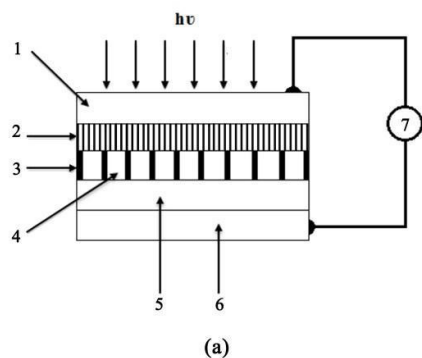


Figure.1(a) - Schematic structure of Cu/n-Cu₂O/R-C₁₈/p-CuI/CNT DSSC. 1- Conductive glass, 2- CNT thin layer, 3- R-C₁₈, 4- p-CuI colloidal particles, 5- n-Cu₂O, 6- Cu and 7- load.

Fig.1(b) - Molecular structure of the Octadecyl Rhodamine (R-C₁₈) dye molecule used in this experiment.

Well cleaned Cu plates (1cm x 3cm) were immersed in a 10⁻³M CuSO₄ solution and boiled till a layer of Cu₂O was appeared on the surface. The amount of Cu₂O was controlled by the boiling time. During the boiling, a fixed volume of CuSO₄ solution was

maintained to provide the same experimental conditions for different preparations. Best n-Cu₂O layer was prepared on the boiling time of 60mins.

A solution of CuI was prepared by dissolving 5mg of CuI in 10ml of moisture-free acetonitrile. CuI colloidal solution was lightly spread on the Cu/n-Cu₂O surface to fabricate the Cu/n-Cu₂O/CuI photoelectrode.

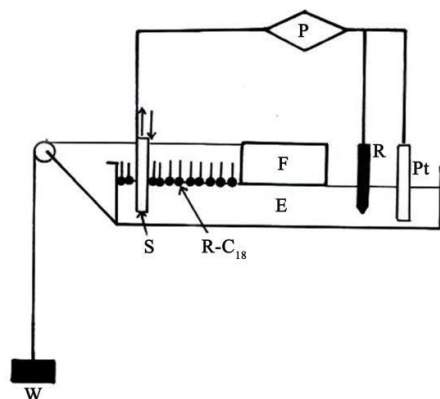


Figure.2 - P- potentiostat, R- reference electrode, Pt- platinum counter electrode, E- electrolyte, F- floater, W- weight and S- Sample.

The R-C₁₈ dye as shown in Fig.1(b) was deposited on the Cu/n-Cu₂O/p-CuI electrode by using the LB technique. Experimental setup used for LB deposition is shown in Fig.2. A constant voltage was applied to the Cu/n-Cu₂O/p-CuI electrodes using the conventional potentiostatic method with the three-electrode configuration during the deposition of LB films as shown in Fig.2. A Pt wire and an Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. (10⁻²M) Fe²⁺/Fe³⁺ (10⁻²M) and 1 × 10⁻²M NaH₂PO₄-Na₂HPO₄ pH = 6 buffer solution was used as the electrolyte for LB deposition. Several drops of chloroform (10⁻⁴M) of dye were placed onto the electrolyte surface; then the monolayer dye film was compressed to the surface pressure of 35 dyn cm⁻¹ at 20–23°C. The monolayers were transferred by a vertical dipping method onto the Cu/n-Cu₂O/p-CuI surface [10].

A thin CNT layer was deposited on the Cu/n-Cu₂O/Dye/p-CuI photoelectrode. ITO coated glass plate was placed on Cu/n-Cu₂O/Dye/p-CuI/CNT photoelectrode to fabricate Cu/n-Cu₂O/Dye/p-

CuI/ITO solid state photovoltaic as shown in the Fig.1.

E. Experimental techniques

Absorption properties were determined by Shimadzu 1800 UV Spectrophotometer. Analytical grade chemicals and double distilled water were used for the experiment. Photocurrent spectra were measured with an applied physics monochromator. A 100W tungsten filament lamp was used as the light source and water circulated perspex cell was used to cut off the IR radiation of the light source.

Photocurrent quantum efficiency ($\Phi\%$) is calculated from the following equation .ie $\Phi\% = [\text{number of electrons created}/\text{number of photons incident}] \times 100$

III. RESULTS AND DISCUSSION

F. The variation of $\Phi\%$ with number of R-C₁₈ LB films deposited in the PEC with Cu/n-Cu₂O/R-C₁₈/p-CuI photoelectrodes

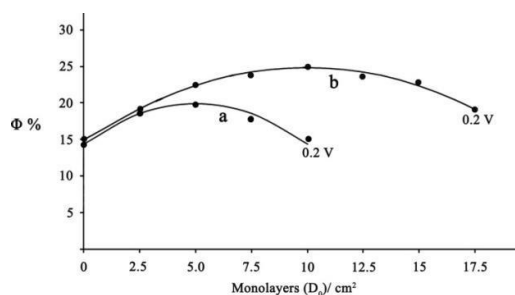


Fig.3 – The variation of the quantum efficiency ($\Phi\%$) with number of R-C₁₈ LB monolayers deposited at +0.2V vs Ag/AgCl positive applied potentials in the presence of (10^{-3}M) $\text{Fe}^{2+}/\text{Fe}^{3+}$ and (10^{-2}M) $\text{NaH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$, pH=6 buffer solution, at $\lambda=560\text{nm}$.

Fig.3 shows the variation of the photocurrent quantum efficiency ($\Phi\%$), with number of R-C₁₈ monolayers deposited on Cu/n-Cu₂O/p-CuI (curve a) and after applying CNT on top of the Cu/n-Cu₂O/R-C₁₈/p-CuI films (curve b) in the DSSC as discussed in the experimental part. It is clearly seen that an enhancement of the photocurrent and optimum surface concentration (D_{op}) of R-C₁₈ LB films occurs after applying CNT on top of the Cu/n-Cu₂O/R-C₁₈/p-CuI cell. Maximum photocurrent quantum efficiency reached was $\approx 20\%$ at +0.2V vs Ag/AgCl before applying CNT and after it became to 25%. The reason for the photocurrent enhancement and the increment of the optimum surface concentration because of the CNT serves as an upper electrode to

collect photo-generated charge carriers suppressing the energy dissipative process, associated with the device.

G. Diffuse reflectance Spectra

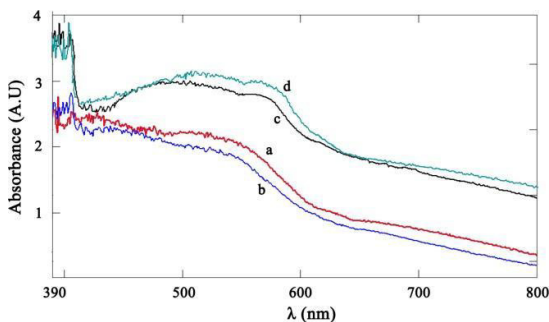


Fig.4 - Diffuse reflectance spectra of (a) Cu/n-Cu₂O, (b) Cu/n-Cu₂O /p-CuI (c) Cu/n-Cu₂O /R-C₁₈/p-CuI, (d) Cu/n-Cu₂O /R-C₁₈/p-CuI/CNT

Fig.4 shows the diffuse reflectance spectra of Cu/n-Cu₂O (curve-a), Cu/n-Cu₂O/p-CuI (curve-b), Cu/n-Cu₂O/R-C₁₈/p-CuI (curve-c) and Cu/n-Cu₂O/R-C₁₈/p-CuI/CNT (curve-d). Absorption edge nearly 620nm is due to the light absorption of the band to band transition of n-Cu₂O as shown in (curve a). According to the (curve b) absorption edge nearly 420nm is due to the light absorption of the band to band transitions of p-CuI and 620nm is corresponding to Cu₂O. It should be mentioned that the light absorption characteristics can be observed for both n-Cu₂O and p-CuI of the p-n junction photoelectrode confirming the formation of p-CuI on n-Cu₂O surface. According to the (curve c) distinct absorption edges for n-Cu₂O, p-CuI and absorption peak near to 560nm for dye absorption can be observed. It should be mentioned that the dye absorption peak 560nm red shift to 570nm for the device with CNT (curve d). The red shift may be due to the CNT attachment to the R-C₁₈ dye layer. It should be mentioned that no transformation has been made by introducing CNT and CNT only serves as an upper electrode to collect photo-generated charge carriers. The estimated band gap from the absorption edges corresponding to the light absorption of p-CuI was $\approx 3.1\text{eV}$ ($\lambda \approx 410\text{nm}$), n-Cu₂O was $\approx 1.9\text{eV}$ ($\lambda \approx 640\text{nm}$) and in the case of R-C₁₈ clear peak can be observed at 560.

H. Photocurrent Action Spectra

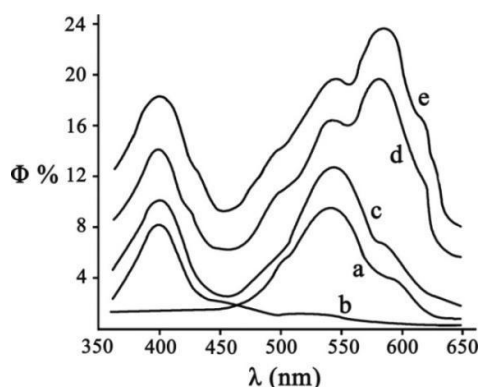


Fig.5 - Photocurrent action spectra of (a) Cu/n-Cu₂O, (b) Cu/p-CuI, (c) Cu/n-Cu₂O /p-CuI (d) Cu/n-Cu₂O /R-C₁₈/p-CuI and (e) Cu/n-Cu₂O /R-C₁₈/p-CuI/CNT

Fig.5 (curve a) and (curve b) show the photocurrent action spectra for Cu/p-CuI and Cu/n-Cu₂O electrodes respectively. Distinct peaks were appeared 420nm and 620nm for (curve a) and (curve b). Both peaks were appeared in (curve c) according to the Cu/n-Cu₂O/p-CuI cell and a photocurrent enhancement can be observed due to n-Cu₂O/p-CuI junction effect. In (curve d), distinct photocurrent peaks can be observed due to n-Cu₂O, p-CuI and sensitized photocurrent due to sensitization of R-C₁₈ with CuI. A red shift observed for the (curve e) due to CNT layers with compared to that of the photoelectrode without CNT and photocurrent enhancement can be observed due to effect of efficient charge separation of the photogenerated charge carriers through CNT.

I. I-V characteristics of solid state devices

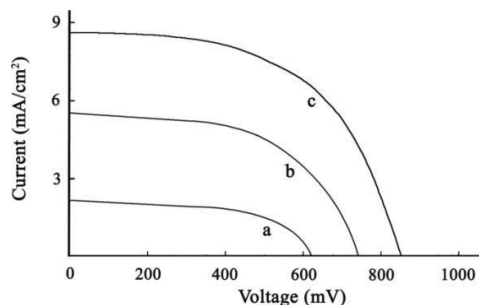


Fig.6 - I-V characteristics of the a-Cu/-Cu₂O/p-CuI, b-Cu/n-Cu₂O/R-C₁₈/p-CuI and c-Cu/n-Cu₂O/R-C₁₈/p-CuI/CNT solid state photovoltaic devices

Fig.6 shows the I-V characteristics of (a) Cu/n-Cu₂O/p-CuI, (b) Cu/n-Cu₂O/R-C₁₈/p-CuI and (c) Cu/n-Cu₂O/R-C₁₈/p-CuI/CNT solid state devices. The device fabricated with the Cu/n-Cu₂O/p-CuI cell

shows a short-circuit photocurrent ($I_{sc} \approx 2 \text{ mA cm}^{-2}$), and open-circuit voltage ($V_{oc} \approx 600 \text{ mV}$) and maximum power conversion efficiency $\approx 1.5\%$. The values obtained for Cu/Cu₂O/R-C₁₈/p-CuI cell are $I_{sc} \approx 5.5 \text{ mA cm}^{-2}$ and open-circuit voltage $V_{oc} \approx 700 \text{ mV}$ and maximum power conversion efficiency $\approx 2.5\%$. After adding CNT for Cu/Cu₂O/R-C₁₈/p-CuI cell, $I_{sc} \approx 8.6 \text{ mA cm}^{-2}$, and open-circuit voltage $V_{oc} \approx 840 \text{ mV}$ and maximum power conversion efficiency $\approx 4\%$. The higher values of cell parameters (V_{oc} and I_{sc}) were obtained efficient charge separation due to the CNT.

J. Time development of the Photocurrent

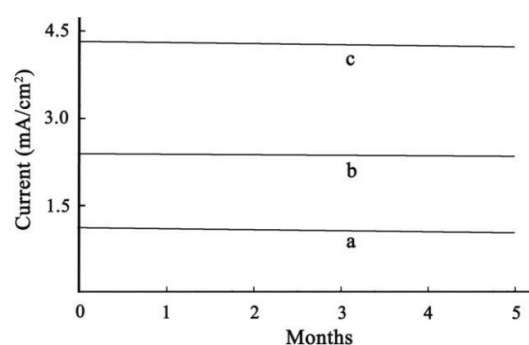


Fig.7- Time development of the photocurrent in the a-Cu/-Cu₂O/p-CuI, b-Cu/n-Cu₂O/R-C₁₈/p-CuI and c-Cu/n-Cu₂O/R-C₁₈/p-CuI/CNT solid state photovoltaic devices.

Time development of the photocurrent under visible light is shown in Fig.7. Remarkable stability can be observed in every cell and the steady state photocurrent increases when adding R-C₁₈ dye to Cu/n-Cu₂O/p-CuI cell and further enhanced due to adding CNT. Dye layer was performed by enhancing agent of light absorption during the photocurrent generation process. CNT facilitates to move the excited electrons from Cu/n-Cu₂O/R-C₁₈/p-CuI to ITO plate to separate photo-generated after absorbing the light. So that the recombination of photo-generated charge carries is suppressed. CNT penetrated in the p-CuI layer can act as collection centres to transfer the photo-generated carries into the circuit to flow the photocurrent. This proves that the CNT was serving as an upper electrode for this particular photovoltaic cell.

IV. CONCLUSION

A solid state thin film photovoltaic cell produced with CNT and Cu/n-Cu₂O/R-C₁₈/p-CuI for the first time. The photocurrent enhancement was observed

in Cu/n-Cu₂O/R-C₁₈/p-CuI/CNT and compared with Cu/n-Cu₂O/R-C₁₈/p-CuI photoelectrodes. The photocurrent increases when the Contact between Cu/n-Cu₂O/R-C₁₈/p-CuI and ITO was increased and it serves as upper electrode. Remarkable stability was observed in the Cu/n-Cu₂O/R-C₁₈/p-CuI/CNT/ITO solid state photovoltaic cell.

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¹RDA Rajapaksha is a Ph.D. research student of Department of Electronics, Faculty of Applied Sciences of Wayamba University of Sri Lanka. His research interests include fabrication of semiconductor base electronics devices using Nanotechnology. He has produced 9 international and local Journal publications and conference proceedings to his credit. He had been a Temporary Demonstrator of Department of Electronics since April, 2011 to April, 2013.



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