

B. SUMMARY

Title: High efficiency photovoltaic cells related to p-CuSCN, p-CuI, n-TiO₂, n-Cu₂O sensitized with ordered and disordered molecular arrangements, at low cost

Research Institute: Physics Department
Ruhuna University

Chief Scientific Investigator: Dr C A N Fernando

Period of contract:

Two years (2nd September 1996- 2nd September 1998)

Scientific Background and Scope/Objectives of Project:

Dye sensitization associated with photovoltaic cells using ordered or randomly distributed molecular arrangements has become an object of attention for many workers as it is a technique that might be adopted for use in solar energy conversion devices at low cost.

Dye sensitization extends the spectral response of photovoltaic cells based on wide band gap semiconductors. Determination of new phenomena related to dye sensitized photovoltaic cells with ordered molecular arrangements, and investigations of high efficiency

photovoltaic cells with new photocurrent generation mechanisms for practical purposes with disordered and ordered molecular arrangements are the main objectives from this investigation.

Experimental Method:

Well cleaned copper plates were immersed into a acetonitrile solution (1M) containing 5mg CuI power dissolved to deposit p-CuI on copper plate. To deposit dyes, colloidal p-CuI deposited copper plates were immersed into (10^{-2} M) dye solutions. Rhodamine Iodide was deposited as the first dye on p-CuI semiconductor by simple dipping method. R-I deposited p-CuI photoelectrodes, were immersed into a CV dye solution to deposit CV on R-I as the second dye. The dyed plates were immersed in a solution (pH 6.0) containing 0.1M potassium citrate and 10^{-5} M chloroplatinic acid to platinized the dye layers. Electrolyte used was KI (10^{-2} M) + I₂ (10^{-4} M) solutions. Light intensity measurements were done by using an International

Light II 700 radiometer. 500W tungsten filament lamp was used for the illumination. Hokuto Denko potentiostat was used with three electrode configuration for the photocurrent measurements. Applied photophysics monochromator was used to measure the photocurrent action spectra. Photocurrent quantum efficiency (ϕ %) is calculated from the following definition .ie

$$\phi\% = (\text{no. of electrons created}/\text{no. of photons incident}) \times 100$$

p-CuSCN on conductive glass plates ($100\Omega/\square$) was prepared by evaporation of p-CuSCN powder. Several drops of a chloroform solution ($2 \times 10^{-4}\text{M}$) of the dyes having C-₁₈ carbon chains were placed onto an aqueous subphase of water distilled from deionized water (pH=6.0), then the monolayer dye film was compressed to the surface pressure of 35 dyn/cm at 20-23C° by Langmuir-Blodgett technique to make LB films. Fluorescence spectra were performed using shimadzu RF-540 spectrofluorometer. A well cleaned copper plate (2cmx5cm)

(99.0% purity) was boiled in a 10^{-4} M copper sulfate solution for 15mins to obtain n-Cu₂O on the copper substrate.

A conductive glass plate ($100 \Omega/\square$) was employed to the dye absorbed n-Cu₂O/p-CuSCN junction as the upper contact in order to make the solid state cell. A Shimadzu RS-540 instrument was used for the photoluminescence measurements.

Results Obtained:

Colloidal p-CuI deposited on copper substrates are sensitized with a double dye system, Rhodamine Iodide (R-I) and Crystal Violet (CV). Rhodamine Iodide is deposited on colloidal p-CuI as the first dye before depositing the 2nd dye Crystal Violet on Rhodamine Iodide and a photocurrent quantum efficiency enhancement can be observed. Clearly two peaks can be observed in the photocurrent action spectrum of the double dye system.

A remarkable stability in a sharp photo-current peak (570nm) was found sensitizing p-CuSCN semiconductor with double dye

LB films of Rhodamine-C₁₈ (R-C₁₈) monolayers and Methylviolet-C₁₈ (M-C₁₈) monolayers. A remarkable stability of the steady state photo-current quantum efficiency calculated correcting to the dye absorption (quantum efficiency of 45% at 570nm) in the sharp photo-current peak was obtained in (10⁻² M) KI + (10⁻⁴ M) I₂ aqueous solution of pH= 6.5. Photocurrent enhancement is due to an operation of an interaction. A stable solid state photovoltaic cell was made by sandwiching crystal violet dye between n-Cu₂O prepared on a copper substrate and p-CuSCN transparent thin film prepared on n-Cu₂O. Hexagonal crystals can be obtained as observed from SEM pictures. A strong rectification character can be observed for the junction photoelectrode with n-Cu₂O and p-CuSCN. After sandwiching crystal violet dye between n-Cu₂O and p-CuSCN a photocurrent enhancement can be observed clearly with compared to the solid state photovoltaic cells made with bare n-Cu₂O, n-Cu₂O/p-CuSCN and dye deposited p-CuSCN.

Surface states on p-CuSCN are sensitized by aggregated crystal violet in addition to the cathodic sensitization process between semiconductor valence band and the excited monomeric dye molecules. Photocurrent quantum efficiency obtained for the aggregated dyes sensitized the surface is 25% at $\lambda = 460$ nm, and 14% for the monomeric dyes at $\lambda = 580$ nm.

Conclusions:

Colloidal p-CuI sensitized double dye system brings new photocurrent generation mechanisms to enhance the photocurrent quantum efficiency. Platinization of these dyes enhances the photocurrent quantum efficiencies considerably clearing the photocurrent generation mechanisms. Stable higher photocurrent quantum efficiency (45%) was obtained in the steady state with compared to the presently available dye sensitized solar cells for an ordered molecular arrangement prepared by Langmuir-Blodgett technique using Methyl Violet-C₁₈ and Rhodamine-C₁₈. The stability of the photocurrent peak is extremely high with the double

dye since the photocurrent generation process occurs due to an operation with an interaction. A dye sensitized solid state photovoltaic cell was made by sandwiching crystal violet dye between n-Cu₂O and p-CuSCN thin films. A photocurrent enhancement was observed for this solid state photovoltaic cell with compared to that of the solid state photovoltaic cells made from bare n-Cu₂O, n-Cu₂O/p-CuSCN and dye deposited p-CuSCN. The reason for the photocurrent enhancement is due to the efficient charge separation process provided by the junction photoelectrode. A remarkable stability was observed in the time development of the photocurrent. However the efficiency reached is nearly 0.1%. Dye sensitization by participation of surface states on p-CuSCN photocathode was found for the first time. Here, surface states take part to obtain a higher photocurrent quantum efficiency for p-CuSCN. A sharp photocurrent peak was observed in the photocurrent action spectra ($\lambda_{\text{max}}=460\text{nm}$) for aggregated crystal violet dyes. Maximum photocurrent quantum efficiency reached is 25%.

Papers Published on Work Done under the contract

1. C A N Fernando, I Kumarawadu, K Takahashi, A Kitagawa
and M Suzuki

Crystal Violet dye sensitized photocurrent by participation
of surface states on p-CuSCN

Solar Energy Materials and Solar Cells. 58(1999)337-347

2. C A N Fernando and I Kumarawadu

Colloidal p-CuI sensitized double dye system

Semiconductor Science Technology (Submitted)

3. C A N Fernando, M Suzuki and A Kitagawa

The highest photocurrent quantum efficiency with
Langmuir-Blodgett films on p-CuI dye sensitized solar cell.

Proceedings of the International Work Shop on Low Cost

Electronic Materials and Solar Cells, Colombo, Sri Lanka, 5-

6 March 1997, page-73

4. C A N Fernando

Photo-current generation of anodically sensitized photo-electrochemical cells

Symposium on a energy Policy for Sri Lanka,07-08 March, 1997. Open University Review of Engineering Technology, page-41

Presentations/ Rg/96/p/05

1. C A N Fernando and L A A de Silva

Enhanced photocurrent with p-Cu₂O photochemical cell
Sri Lanka Association for the Advancement of Science.

53rd Annual Session-1997, Proc. Part 1. E1-04, page-291

2. C A N Fernando and S K Wethasingha

A simple photoelectrochemical cell

Sri Lanka Association for the Advancement of Science.

53rd Annual Session-1997, Proc. Part 1. E1-14, page-301.

3. C A N Fernando, L A A de Silva, P D Anurasiri
M S W de Silva
p-Cu₂O photocathodes with Langmuir-Blodgett films of
merocyanine
Sri Lanka Association for the Advancement of Science.
53rd Annual Session-1997, Proc. Part 1. E2-29, page-353.
4. C A N Fernando and I Kumarawadu
Colloidal p-CuI sensitized double dye system
Sri Lanka Association for the Advancement of Science.
53rd Annual Session-1997, Proc. Part 1. E2-47, page-371.
5. C A N Fernando, I Kumarawadu and D T S de Silva
Sensitized photocurrent with a surface state in p-CuSCN
photocathode
Sri Lanka Association for the Advancement of Science.
53rd Annual Session-1997, Proc. Part 1. E2-49, page 373.

6. C A N Fernando, S K Wethasingha, R M Mehra, N C Mehra, V Agrawal
A study of photoluminescence measurements and scanning electron micrograph of n-Cu₂O photoelectrodes
Sri Lanka Association for the Advancement of Science.
54th Annual Session-1998, Proc. Part 1. E1-08, page 235.
7. C A N Fernando, T M W Bandara and S K Wethasingha
H₂ evolution from n-type photoresponse of Cu₂O with Fe²⁺/Fe³⁺ redox couple
Sri Lanka Association for the Advancement of Science.
54th Annual Session-1998, Proc. Part 1. E1-09, page 236.
8. C A N Fernando and L A A de Silva
Photovoltaic cell made from merocyanine-C₁₈ Langmuir-Blodgett films on a plastic film
Sri Lanka Association for the Advancement of Science.
54th Annual Session-1998, Proc. Part 1. E1-10, page 237.
9. C A N Fernando, L A A de Silva, R M Mehra, N C Mehra and P C Mathur

Properties of p-Cu₂O semiconductor thin film made between (copper and gold) alloy and Indium Tin Oxide film in a photoelectrochemical cell.

Sri Lanka Association for the Advancement of Science.

54th Annual Session-1998, Proc. Part 1. E1-11, page 238.

10. C A N Fernando, and I Kumarawadu

Relationship for photocurrent quantum efficiency with a number of Langmuir-Blodgett films on p-CuI

Sri Lanka Association for the Advancement of Science.

54th Annual Session-1998, Proc. Part 1. E2-34, page 301.

11. C A N Fernando, I Kumarawadu, P D Anurasiri, A Kitagawa and M Suzuki

Improved photocurrent quantum efficiency from Langmuir-Blodgett films

Sri Lanka Association for the Advancement of Science.

54th Annual Session-1998, Proc. Part 1. E2-35, page 302.

12. C A N Fernando, W T C Priyankara, A Kitagawa and M Suzuki

Application of interlocked Langmuir- Blodgett films on
p-CuSCN with sensitized photocurrent

Sri Lanka Association for the Advancement of Science.

54th Annual Session-1998, Proc. Part 1. E2-37, page 305.

13. C A N Fernando, T M W Bandara, R M Mehra, N C

Mehra, P C Mathur and S Shuckla

A simple technique to obtain cuprous oxide hexagonal
crystallites for solar energy conversion devices

Sri Lanka Association for the Advancement of Science.

54th Annual Session-1998, Proc. Part 1. E2-39, page 306.

Part C.

One reprint and the references are given for the presentations

And published papers at the end of part B.

Part D.

Two Master of Philosophy theses are provided

under the contract, for the two research assistants.

Now one post graduate thesis is already submitted and the
other is in the writing stage.