Investigations of Photophysical and Photochemical Processes in p-CuSCN Photoelectrochemical Cells Sensitized with Langmuir-Blodgett Films

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学位の種類	博士（学術）
学位記番号	博甲第153号
学位授与の日付	平成7年9月26日
学位授与の要件	課程博士（学位規則第4条第1項）
学位授与の題目	INVESTIGATIONS OF PHOTOPHYSICAL AND PHOTOCHEMICAL PROCESSES IN p-CuSCN PHOTOELECTROCHEMICAL CELLS SENSITIZED WITH LANGMUIR-BLODGETT FILMS （ラングミュアーブロジェット膜による光増感 p-CuSCN 光電気化学セルの光電変換過程の研究）
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学位論文要旨

Introduction The energy falling on the earth's surface, after absorption and scattering by the atmosphere, is $3x10^{24}$ joules per year, corresponding to an average power availability of 10^{17} watts. The present consumption of primary energy in all forms by mankind is 2×10^{20} joules per year. If we were able to collect and use solar energy with an efficiency of 10%, the available solar energy would still exceed future requirements by a factor of 150 (1, 2).

In recent years, considerable interest has been focussed on the development of systems capable of collection and storage of solar energy (3, 10). Amongst the numerous systems that can envisage, photoelectrochemical processes are receiving extensive and careful scrutinity all over the wold (3-10).

The conversion of solar radiation into electricity by means of the silicon photovoltaic cell is at present the most sophisticated technical development in solar energy devices (1, 2). The silicon cell, which was developed for powering space vehicles and satellites is still the most efficient and reliable. Unfortunately, the manufacture of pure silicon crystals is very expensive, and electrical power from silicon photovoltaic cells costs about a hundred times more than conventional electrical power.

Dye sensitization of semiconductor-electrolyte interfaces 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 (7, 11-15). Dye sensitization extends the spectral response of photoelectrochemical cells based on high band gap materials (11-15). The familliar high band gap semiconducting materials, e.g, GaP, $SrTio_3$ or other oxide semiconductors are not the best materials for

studying dye sensitization because of poor dye adsorption.

In earlier reports, it was exhibited that CuSCN (a p-type semiconductor of band gap~ 3.2 eV) is an ideal, and chemically stable material for studying dye sensitization (15-20). Unfortunately, these dye sensitized systems suffer from many problems since the deposited dyes have random molecular arrangements on p-CuSCN. Investigations of photophysical and photochemical processes associated at Semiconductor/Dye-Electrolyte Interface is limitted, if the deposited dyes have random molecular arrangements.

The Langmuir-Blodgett (LB) technique is extremely attractive (25-27) as a tool in making ordered molecular arrangements on various materials. Investigations related to the dye sensitization of p-CuSCN with ordered molecular arrangements are not reported in the Literature. This study describes, for the first time, the behaviours of p-CuSCN based photoelectrochemical cells sensitized with ordered molecular arrangements deposited by LB technique.

Chapter 2 to Chapter 3 illustrate the theoretical back ground of this research.

Chapter 4 present some previous works related to structural behaviors of p-CuSCN, semiconductor properties of p-CuSCN, photocatalytic properties of p-CuSCN polycrstalline powder and dye sensitized photoelectrochemical cells and solid state photovoltaic cells with random molecular arrangements of various dyes.

From Chapter 5, the formation of surface states in the p-CuSCN photocathodes, kinetics of photocurrent generation and photophysical properties associated at semiconductor/ Dye-Electrolyte Interface, electrolyte dependence for the p-CuSCN PECs sensitized with ordered molecular arrangements of Rhodamine-C_{18} LB films, absorption properties of Methylviolet and Rhodamine dye solutions and solid samples deposited on glass plates by LB techniques and simple dipping techniques, variations of absornace and photocurrent with the angle of polarized plane of incident light, stabilization of p-CuSCN PECs and a mechanism involved to generate a sharp photocurrent enhancement sensitized with Methylviolet-C_{18} and Rhodamine-C_{18} double dye LB films are illustrated in details.

Surface states in p-type Cu^{I} thiocyanate (CuSCN) were detected from I-V characteristics, diffuse reflectance spectra, and photocurrent action spectra. The p-CuSCN films are sensitized by Rhodamine with Octadecyl-alkyl chain, and the sensitized photocurrent is observed with the visible light illumination. Inspite of the surface states in p-CuSCN, the maximum photocurrent quantum efficiency (ϕmax) at λ=570nm, in ($1x10^{-4}$M) KI+I_2 solution, pH=6, reached ~8.6%, where the surface concentration of the photocathode Cu/ p-CuSCN/Dye was $1.1x10^{14}$ molecules cm^{-2}. Photocathodes were biased at -0.25V vs AgCl/ Ag to give a zero dark current. From the variation of values with the reduction potential of electron acceptors, the cathodic sensitization mechanism presented is further confirmed.

The rate equations for the photoinduced charge transfer processes at the sensitized interface are solved to obtain an expression for the steady state photocurrent quantum efficiency, as a function of rate constants of the photophysical and photochemical processes at Semiconductor/Dye-Electrolyte interface, deposited dye concentrations, concentration of the electron acceptor in the electrolyte.

It was found that the photocurrent quantum efficiency of photoelectrochemical cells with p-CuSCN photocathode sensitized with double dye layers such as Rhodamine-C_{18} and Methylviolet-C_{18} is greatly enhanced (~15%), when the double dye system is prepared using

Langmuir-Blodgett (LB) technique. An ordered arrangement of dye molecules in LB films provides a suitable condition to transfer photogenerated holes and electrons between two dye layers, so that photogenerated holes upon excitation can transfer effectively into the valence band of p-CuSCN.

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学位論文の審査結果の要旨

A.N. Fernando 氏は，約 3.2eV のバンドギャップを有するｐ型の CuSCN 半導体を電極として用いた Photo-electrochemical cell の研究を行った。この材料を選んだのは化学的に安定であること，色素増感の可能性を考慮してのことである。まず，CuSCN を銅基板の上に作成する技術を開発し，これを用いた Photo-electrochemical cell を構成しその光電特性を調べた。このセルに対して可視域に光電感度を持たすためにローダミンを用いた色素増感の方法を試み，2.2eV 付近に大きな光電感度を得た。色素膜を形成する方法には浸積法やラングミュア・プロジェッド法（LB 法）を試み，LB 法で堆積した膜の場合に増感効果が大きくなることを見出した。

この結果を基に，更なる光電変換効率の向上を目指して２重色素層増感に挑戦した。２種類の色素としてローダミン及びメチルバイオレットを用い，p-CuSCN の上に LB 法でメチルバイオレット／ローダミンの順で堆積した試料で期待通り大幅な光感度の増大を観測した。しかも～570nm 付近で光電流が鋭いピークを持ち量子効率は15%に達するという目覚ましい結果を得た。

顕著な量子効率の向上が得られる原因として，LB 法で作成した色素膜は分子が規則的に配列し，分子軌道の規則的な重なりが生じること，そのためメチルバイオレットでは高エネルギー側の副吸収帯が主吸収帯に替わることなどを見出し，これによって２種の色素の HOMO と LUMO の位置関係が電荷分離に好都合な状況が作られ量子効率の改善が起こると結論している。

以上の結果は，学術的に価値の高いものであり，学術博士の学位に値すると言える。