An Enhancement of Efficiency of Photo-Electrochemical Cell by Coupling Multiple Dyes

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Abstract *- Sensitization process of triscarboxy-ruthenium terpyridine"[Ru(4,4',4"-(COOH)3-terpy)(NCS)$_3$], indoline D358 and their mixtures on ZnO films were studied by means of utilization as light harvesting electrodes in photo-electrochemical cells. An enhancement of the efficiency of the cell was observed by coupling of these dyes compare to that of individuals. The maximum power conversion efficiency of 3.7 % was obtained for ZnO based photo-electrochemical cells.*

Indexed Terms *- black dye, dye cocktails, indoline D358 dye, power conversion efficiency.*

I. INTRODUCTION

An investigation of photo-performance on the silver halide electrodes open the mind of new field so-called dye sensitization [1]. Sincethen, massive work has been carried out in this field. Fabrication of dye-sensitized solar cell with the efficiency over 10% by a Swiss research group is the breakthrough of this field [2]. Organic dyes and natural pigments have been used by aiming of fabrication of environmentally friendly solar cells. However, achieved efficiencies of these cells were less than that of solar cells with metal centered dyes [3-10]. Improving of efficiency of solar cell is one of the scientific hurdles. Recently, enhancement of the performance of dye-sensitized solar cells (DSSCs) was achieved by modifying the morphology of the light-harvesting electrode [11]. An appropriate coupling of dyes is another technique to improve the efficiency of the cell as extending absorption properties of light harvesting electrode as matching with the solar spectrum. Matching of LUMO levels of dyes play major role in such a cell. Several attempts have been made to extend photo-response of solar cells by coupling dyes and natural pigments [12-15]. In most cases, nano-porous TiO_2 was used as the substrate of the cell. In the present work, ZnO is chosen as the substrate since ZnO has higher electron mobility than TiO_2 expecting similar or higher performance of the cell compare to that of titania based DSSCs. The maximum photocurrent of 17.1 $mAcm^{-2}$ with the efficiency of 3.7 % was observed for DSSCs fabricated by coupling of D358 dye with triscarboxy-ruthenium terpyridine" [Ru(4,4',4"-$(COOH)_3$-terpy)$(NCS)_3$] (Black dye) compare to that of dyes in individually.

II. EXPERIMENTAL SECTION

A 0.65 g of ZnO nano powder (Wako) was grinned with 0.25 ml of glacial acetic acid and 0.25 ml of Triton X-100. The paste was transfer to 40 ml of ethanol and was sonicated for 15 min. Resulting semi-colloidal suspension was sprayed on to the fluorine-doped conduction glass plate (FTO, 1 x 2.5 cm^2) at 150℃. ZnO coated glass plate was fired at 450℃ for 30 min. Loosely bounded crust was removed by wiping ZnO film smoothly by a piece of cotton wool. The thickness of the ZnO film was successively achieved as 8 μm. Dyes D358 (Mitsubishi paper mills limited, Japan) and Black dye (Solaronix) were used as purchased. Stock solutions of Black dye and D358with the concentration of ~10^{-4} M were prepared by dissolving dyes in a mixture of acetonitrile, tert-butylalcohol 1:1 by volume and dry ethanol, respectively. Dye was coated on ZnO electrodes as follows : ZnO coated glass plates were kept immersed in the dye solution and the temperature of the dye solution was maintained at 40℃. Varying immersion time in dye solutions is

controlled dye concentration on ZnO electrodes. Multiple coatings of dyes were carried out by coating second dye after coating the first dye on ZnO electrode.A Pt coated conducting glass plate was used as cathode.ZnO coated electrode and Pt coated electrode were sandwiched as ZnO layer and Pt coated layer overlap. The space between two electrodes was filled with an electrolyte (0.1 M LiI, 0.05 M I_2, 0.6 M dimethipropylimidazolium iodide in methoxyacetonitrile). Photo-effects of the cell were studied by illuminating the cell through ZnO layer.

III. RESULTS AND DISSCUSION

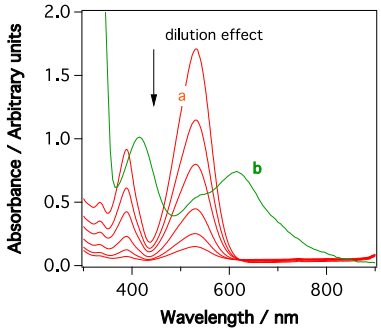

Fig. 1. Absorption spectra for (a) D358, (b) Black dye

Absorption spectrum of D358 is shown as curve a in Fig 1. D358 dye absorbs visible light with the maximum at 532 nm. No significant shift of the spectrum was observed by diluting D358 solution by the same solvent. Thus, indicating no J or H type of aggregates exists in the dye solution. Probably D358 molecules behave as monomers in dry ethanol. Black dye easily dissolved in simple solvents such as ethanol, acetonitrile, tert-butylalcohol. However, dissolution rate of Black dye differs with the solvent. Black dye absorbs visible light in different wavelength regions than D358 with the maxima at 614 nm. Absorption spectrum of Black dye is shown as curve b in Fig 1. Both D358 and Black dye have carboxyl groups and make bonds with ZnO. Formation of bonds with compounds having carboxylic groups and metal oxide is a known factor. Absorption spectra of D358 and Black dye coated ZnO electrodes are shown as in Fig. 2 (curves a and b). In both cases the maxima of absorption band roughly overlap with that of solvent. Absorption spectrum of both dyes coated electrode is shown as curve c in the same figure. Co-absorptionof several dyes at same time is a technique to preparemulti-dye coated electrodes. Specially, in the case of

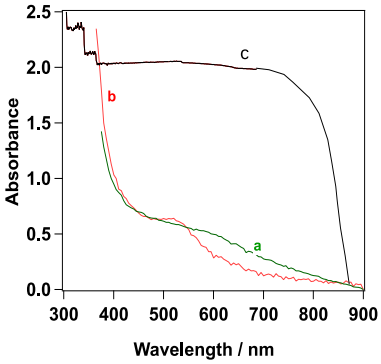

Fig. 2. Absorption spectra for (a) D358|TiO_2, (b) Black dye|TiO_2 and (c) D358|TiO_2Black dye|TiO_2electrode.

co-absorption of different dye molecules preventsaggregation on the electrodes [12]. Electrostatic coupling of each dye is the theory behind by coating several dyes layer-by-layer [13]. Utilization of multi-dye coated electrodes prepared by depositing different dyes; with an alternative semiconductor layer were also studied [14]. In the present study layer-by-layer dye coating technique was used. Dark black color was observed on multi-dye coated electrodes, whereas D358 and Black dye individually coated ZnO electrodes exhibit red and light green, respectively.However, it is difficult to giving an exact description of bonding mechanism of these dyes at the moment of research.

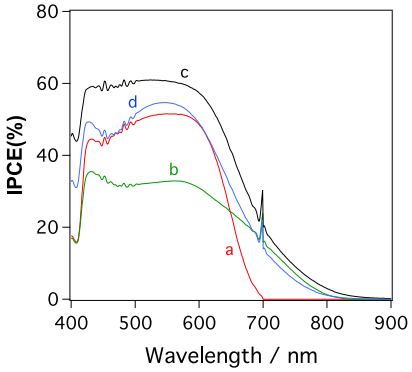

Fig. 3.IPCE spectra for cell composed of (a) D358|TiO_2, (b) Black dye|TiO_2, (c) D358|Black dye|$TiO_2$and (d) Black dye|D358|TiO_2electrode.

IPCE action spectrum of DSSCs with the sensitizer of (a) D358, (b) Black dye, (c) D358|Black dye and (d) Black dye|D358 are shown in Fig. 3. The maximum IPCE of 31, 50, 51 and 60 (%) were achieved for the

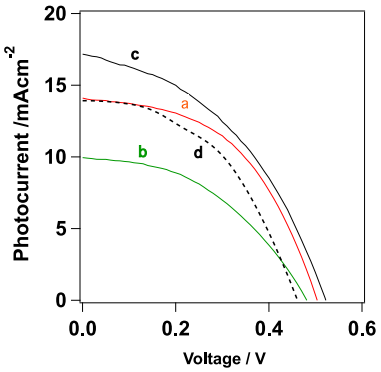

Figure 4 shows the current voltage characteristic of ZnO|dye|electrolyte cells (a) D358, (b) black dye, (c) D358|black dye and (d). black dye|D358

cells prepared by Black dye|TiO_2, D358|TiO_2, Black dye|D358|$TiO_2$and D358|Black dye|TiO_2electrodes.ZnO|D358|electrolyte and ZnO|Blackdye|electrolyte cells exhibited maximum photocurrent of 14.1 and 10.0 $mAcm^{-2}$, respectively. The magnitude of photocurrent of the cells is well agreed with previously published results with same dyes. Self-aggregation of Black dye molecules may be one of the reasons for observed less photocurrent of ZnO|Blackdye|electrolyte cell compared to that of ZnO|D358|electrolyte cell, as is proposed by Ozawa et.al [16].ZnO|D358|Black dye|electrolyte exhibited much higher efficiency of 3.7 % than that of the other cell configurations. Formation of dyad type compound might be one of the reasons for enhanced photo effect of ZnO|D358|Black dye|electrolyte cell [17]. When the order of the dyes reversed lower photocurrent was observed for the cell, probably due to unfavorable energy structure.

CONCLUSION

The maximum power conversion efficiency of 3.7 % was obtained for a ZnO based photo-electrochemical cells by coupling of triscarboxy-ruthenium terpyridine" [Ru(4,4',4"-(COOH)3-terpy) $(NCS)_3$] and indoline D358 dyes.

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