

An enhancement of efficiency of dye-sensitized solar cell by minimizing formation of aggregation of Sq2 dye by co-absorption of N719 dye

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Abstract

Sqaraine 2 (Sq2) and N719 dyes absorb light in different ranges of solar spectrum. Dye-sensitized solar cells (DSSCs) were fabricated using a mixture of Sq2 and N719. Sqaraine dyes form aggregates on TiO₂. Thus the efficiency of the DSSCs made from Sq2 is low. The efficiency of the cell enhances when the Sq2 dye co-adsorbs with N719 dye. This effect is attributed to proper dispersion of Sq2 dye aggregates on TiO₂ electrodes by co-absorption of N719 dye molecules.

Keywords: Sqaraine 2, N719, co-adsorption, aggregates

1. Introduction

Renewable energy is one of the most important scientific and technological challenges in the 21st century. It is evident that photovoltaic cells have been a promising solution as they can convert solar energy into electrical energy [1]. In this regard, dye-sensitized solar cells (DSSCs) have gained considerable attention over the past couple of decades as relatively low-cost and its power conversion efficiency [2]. It has been recently shown that DSSCs with an optimal efficiency of 12%-13% at laboratory scale [3]. Such high conversion efficiencies are a positive sign that DSSCs can be further expanded and compete with traditional silicon-based solar cells. Sensitizers used in such efficient DSSCs are metal centered molecules such as N3 [2], N 907, black dye and N719 [4,5]. In general these dyes have relatively low molar extinction coefficients and generally poor spectral response above 600 nm. The spectral response across full visible range by a single dye has proved very difficult. Thus, dyes having different spectral respond ranges can be incorporated into the sensitizers system to tune the absorption over a broad spectral range. Such co-sensitizing concept has already been practiced using many dyes [6-12]. In this regard, metal centered N719 dye and organic Sq2 are potentially a good combination as N719 harvesting light at wavelength of 400-650 nm and that of Sq2 absorbing wavelength above 650 nm. Light absorption by the dye molecules in the near IR region is very crucial for efficient solar energy conversion. We have shown that N719 dye can be effectively utilized to

disperse the aggregated Sq2 molecules. To the best of our knowledge

this is the first time to attempt to enhance the photoelectric conversion of a sensitizer system in DSSC by reducing the formation of aggregation of Sq2 dye molecules by a N719 dye molecules. This paper reports the light absorption characteristics of pristine dyes, DSSC device fabrication using the N719 co-absorbed Sq2 dye and its device performances.

2. Experimental Section

2.1. Preparation of screen-printing TiO₂ pastes

2.1.1. Nano-crystalline TiO₂ paste

An amount of 12 g of acetic acid was added to 58.6 g of titanium iso-propoxide stirring for 15 min at room temperature. The mixture was poured into 290 mL water, as quickly as possible, with vigorous stirring (700 rpm). The hydrolysis reaction was stirred for one hour. 5.4 mL of 65% nitric acid was added to the mixture and heated from room temperature to 78°C, within 40 min, and peptized for 75 min. Water was added to the mixture. The suspension was kept in a 570 mL titanium autoclave and heated to 250°C for 12 h. 2.4 ml of 65% nitric acid was added and the particles dispersed with a 200 W ultrasonic titanium probe at a frequency of 15 pulses sec⁻¹. The resultant colloidal solution was concentrated with a rotary-evaporator to contain 18% TiO₂. The solution was centrifuged to remove the nitric acid and washed with ethanol three times to produce a precipitate containing 40% TiO₂ in ethanol. An amount of 16 g of TiO₂ precipitate was mixed with 64.9 g of terpineol and a solution of ethyl cellulose in ethanol. The precipitate was well mixed and rotary-evaporated.

2.1.2. Micro-crystalline TiO₂ paste

400 nm particles (in aqueous solution) are transferred into ethanol by repeatedly centrifuging and removing supernatant then topping up with pure ethanol and mixing. 5 parts of 400 nm titania paste and 1 part of 18 nm titania paste were mixed with 3.5 parts of ethyl cellulose and 30.5 mL of terpineol. The mixture was rotary-evaporated until ethanol is removed. More details of preparation of screen-printing TiO₂ paste were published in elsewhere [13].

2.2. Preparation of TiO₂ films

Conducting glass plates (FTO) were cut into 1 x 2.5 cm² pieces, cleaned by detergent, thoroughly washed with distilled water and dried in an oven. One of the edges of FTO (1 x 1 cm²) was covered with 3M tape and placed horizontally on a hotplate facing the conducting side to air. Temperature of the hotplate was gradually increased to 450°C. A solution of titanium diisopropoxide bis(acetylacetonate) (Sigma-Aldrich) in isopropanol (1:9) was sprayed over the FTO quickly at the thermal equilibrium at 450°C and allowed to reach to room temperature by disconnecting power of the hotplate. The microcrystalline TiO₂ paste was coated followed by coating nano-crystalline TiO₂ paste on the compact TiO₂/FTO substrates by screen-printing. The TiO₂ coated films (0.5 cm x 0.5 cm) were backed at 450°C for 30 min. Finally TiO₂ substrates were wetted from a 0.05 M TiCl₄ (aq) in 20% HCl is diluted from a 2.0 M stock solution and again backed at 450°C for another 30 min.

2.3. Dye coating procedure on TiO₂ film

Dyes (Sq2 and N719) used in the present experiment were purchased from well-reputed manufactures and used as purchased. Dyes were dissolved in dry acetonitrile (specially if not mentioned in the text) until concentration reaches ~10⁻⁴ M. Dye was coated on TiO₂ electrodes as follows: TiO₂ coated glass plates were kept immersed in a mixture of dye solution (Sq2:N719 20:1) and individual dye solutions, respectively. The temperature of the dye solution was maintained as 40°C. Dye amount on TiO₂ electrodes was controlled by varying the immersion time in the dye solution.

2.4. Assembling of the cell

2.4.1. Preparation of Pt coated electrodes

10 mM H₂PtCl₆ in isopropanol solution was prepared. One drop of this solution was put onto the conductive side of FTO electrode and allows drying. FTO counter electrode (active side up) was inserted into ceramic tube, gradually heated up to 400°C leave for 15 min., allowed to cool electrode. A hole with a diameter of 1 mm was made on the Pt coated FTO electrode.

2.4.2. Preparation of electrolyte solution

An electrolytic solution was prepared by maintaining 0.03 M iodine, 0.5 M 4-tertbutylpyridine, 0.6 M 1-butyl-3-methylimidazolium iodide and 0.1 M guanidinium thiocyanate in a mixture of acetonitrile/valeronitrile 85:15 by volume.

2.4.3. Sealing of the cell

A rectangular hole with the dimension of 0.5 cm x 0.5 cm was made the centre of 1 cm x 1 cm Surlyn film (thickness is 25 μm). This film was placed on the dye coated TiO₂ film as the rectangular hole superimpose with the dyed TiO₂ film (0.5 cm x 0.5 cm). A Pt coated FTO electrode

hole with a diameter of 1 mm was placed on this TiO₂ electrode with the Surlyn film and heated by applying pressure on glass electrodes as Surlyn film melts and adhesive with two electrodes. The electrolyte was filled in to the device from the back hall and hall was sealed.

2.5. Measurements

Absorption spectra of dye solutions and dye coated TiO₂ films were measured by using UV-VIS-NIR spectrometer (Jasco V-570). Morphology of the cell was studied using scanning electron microscope. Photo-effects of the cell were studied by illuminating the cell through TiO₂ layer. The variation of photocurrent of the cell with the wavelength was measured using monochromator (Jasco) coupled with single-phased lock-in amplifier (NF Instrument-5600 A), under constant photon energy illumination mode. Current-voltage characteristics were recorded with a solar simulator (Wacom) coupled with semiconductor parameter analyser (Hewlett Packard HP 4145B), under 1.5 AM condition. Scan speed was maintained as 0.01 Vmin⁻¹. The interfacial electrical properties of the cells were studied natural bias under a three-electrode configuration with the same electrolyte, by using a multi-channeled potentiostat (Princeton Applied Research) coupled with a computer. The charge transfer resistance at the electrolyte–electrode interface was evaluated from EClab software.

3. Results and Discussion

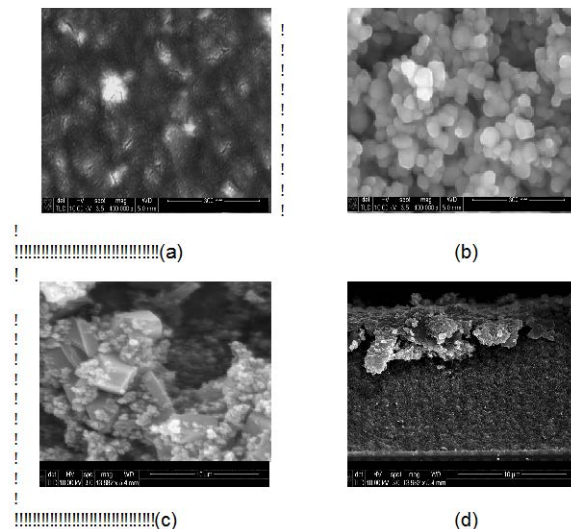


Fig. 1 The morphology of TiO₂ electrodes a) dense TiO₂ layer, (b) nano-crystalline TiO₂ layer and (c) microcrystalline TiO₂ layer and (d) cross section of the electrode.

TiO₂ electrodes used in the present experiment are prepared as producing maximum photo-performance [13]. These TiO₂ electrodes are composed with three

components, namely (a) dense TiO₂ layer, (b) nanocrystalline TiO₂ layer and (c) microcrystalline TiO₂ layer. The morphology of TiO₂ electrodes is shown in Fig. 1. These three layers can be easily distinguished by the nature of the morphology of the layers. The cross-sectional image of the electrode is also clearly indicated that electrode is composed with three layers. The average thickness of the electrode was evaluated as 20 μm from a thickness meter (Fig. 2).

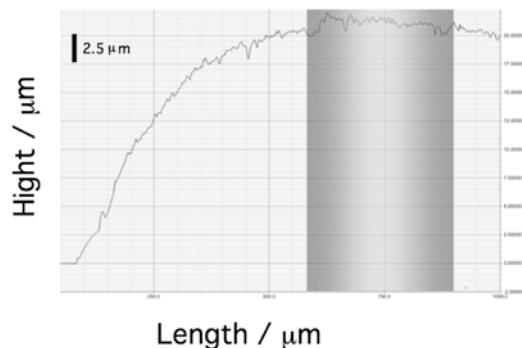
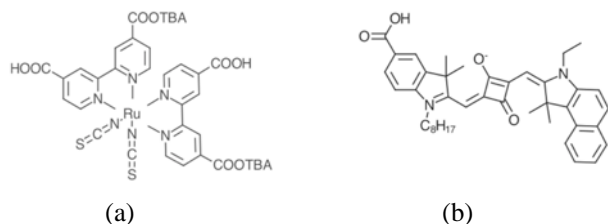


Fig. 2 The variation of thickness of the electrode.



Scheme1. Molecular structures of (a) N719 and (b) Sq2 dyes

Molecular structures of used dyes (a) N719 and (b) Sq2 are shown in scheme 1. Though N719 dye is ruthenium-based dye, Sq2 is an organic dye. Both molecules have carboxylic groups. The solubility of Sq2 is comparably lower than that of N719 dye in organic solvents. Absorption spectrum for (a) N719 and (b) Sq2 are shown in Fig. 3. These two dyes absorb two different wavelength regions with different maxima. The absorption spectrum of Sq2 has red shifted compare to that of N719 dye. The absorption spectra for (c) N719 coated TiO₂ film and (d) Sq2 coated TiO₂ film are also shown in Fig.3. The absorption maxima of both N719 in ethanol and N719 coated TiO₂ film lye at same wavelength (528 nm). However, there is an approximately 25 nm shift in between two absorption maxima of Sq2 (in acetonitrile)

and Sq2 coated TiO₂ film. It is well known that squaraine dyes easily makes H-type aggregates with the solid phases [14]. Therefore, observed 25 nm shifts in Sq2 dye coated TiO₂ electrode most probably due to formation of H-type aggregates.

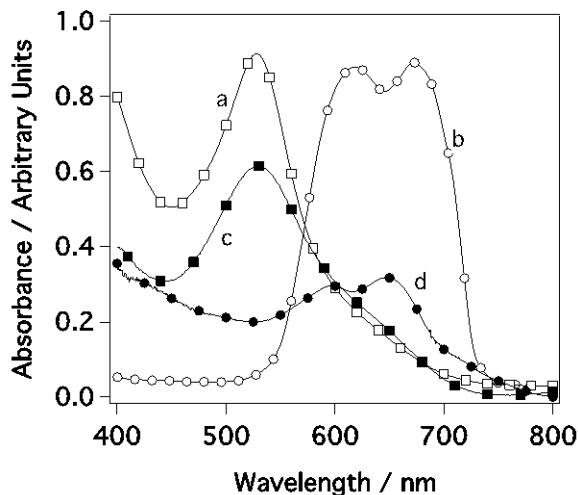


Fig. 3 Absorption spectrum for (a) N719 and (b) Sq2, (c) N719 coated TiO₂ film and (d) Sq2 coated TiO₂ film.

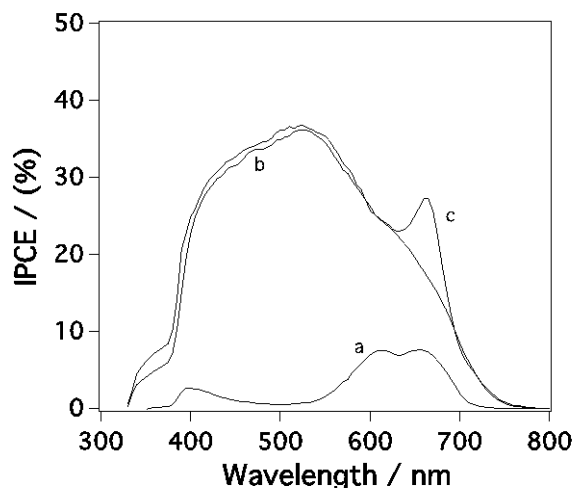


Fig. 4 IPCE action spectra for (a) TiO₂/Sq2, (b) TiO₂/N719 and (c) TiO₂/(Sq2+N719) electrodes in non-aqueous I⁻³⁻ electrolyte

IPCE action spectra for (a) TiO₂/Sq2, (b) TiO₂/N719 and (c) TiO₂/(Sq2+N719) electrodes in non-aqueous I⁻³⁻ electrolyte is shown in Fig. 4. TiO₂/Sq2|electrolyte cell produces lowest IPCE of 7 % among three cell, due to losses of energy via quenching of Sq2 aggregates [14]. TiO₂/N719|electrolyte cell exhibits typical shape of action spectrum with a maximum efficiency at 530 nm.

Enhancement of IPCE in the region of 630 - 695 nm clearly indicates contribution of Sq2 in the photocurrent generation in the mixed dye system. Co-absorption of N719 dye with Sq2 suppresses aggregation of Sq2 dyes on the TiO₂ electrode. Thereby higher photocurrent is generated in the wavelength range of 630-695 nm compare to that of without N719 dye. Thus resulting higher perfor-

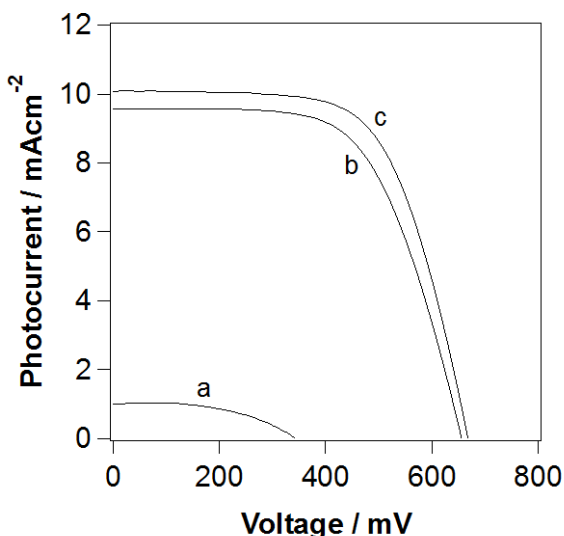


Fig. 5 The IV characteristics of cells made from (a) TiO₂|Sq2, (b) TiO₂|N719 and (c) TiO₂|(Sq2+N719) electrodes.

-mance in the TiO₂|(Sq2+N719)|electrolyte system. Fig. 5 represents the IV characteristics of cells made from (a) TiO₂|Sq2, (b) TiO₂|N719 and (c) TiO₂|(Sq2+N719) electrodes. Higher photo-voltage and photocurrent were observed in multi-dye system than that of individuals.

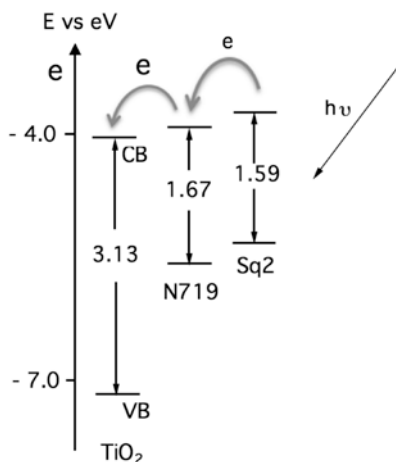


Fig. 6 Photocurrent generation in TiO₂|(Sq2+N719)|electrolyte system under white light irradiation

Photocurrent generation in TiO₂|(Sq2+N719)|electrolyte system under white light irradiation is shown in Fig. 6. The HOMO and LUMO levels of Sq2 and N719 dye were obtained from the work reported by Nattestad et. al. [15]. Polychromatic illumination results electrons in LUMO levels in both dyes. Both dyes could inject photo-generated electrons in to the conduction band of TiO₂ electrode. In addition to that, photo-generated electrons in the LUMO level of Sq2 dye injects to the lower lying LUMO level of N719 dye and then transferred in to the conduction band of TiO₂.

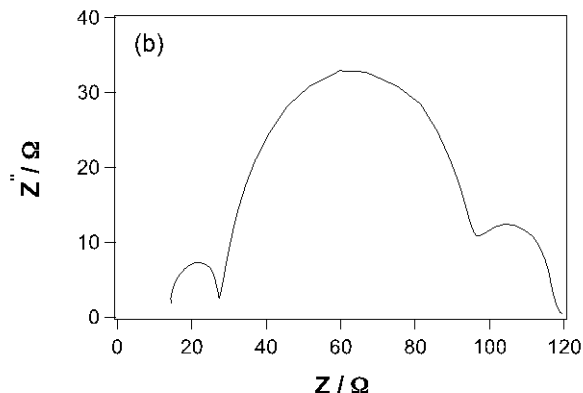
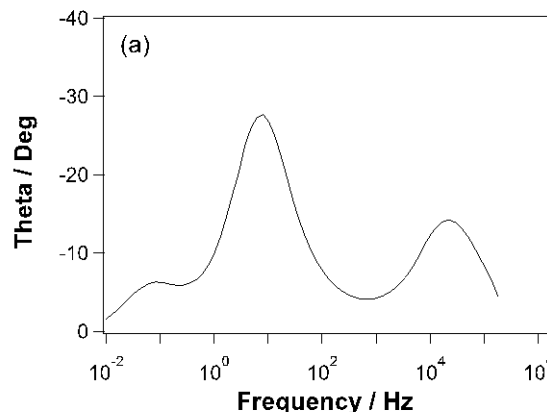


Fig. 7 The cole-cole plot of dye (N719) coated electrode, (a) Bode phase plot and (b) Nyquist diagram.

Internal resistance of the TiO₂ film and the film|substrate interface of TiO₂ films were studied using electrical impedance spectroscopy. Fig. 7 represents the cole-cole plot of multi-dye coated electrode, (a) Bode phase plot and (b) Nyquist diagram. A typical Nyquist diagram for glass based DSCs normally features three semicircles. The semicircle corresponding to the higher range of frequencies (the left semicircle, with diameter R₁), the middle range of frequencies (the middle semicircle, diameter R₂) and the lower range of frequencies (the right

semicircle, diameter R_3) represent I_3^- transport in the electrolyte, electron recombination at the $TiO_2|electrolyte$ interface together with electron transport in the TiO_2 network and the redox reaction at the platinum counter electrode, respectively [16]. The high frequency intercept with the real axis is the ohmic resistance (R_0) and is related with the sheet resistance of the substrate of the working electrode. Values of $R_0 - R_3$ were evaluated as 15, 10, 40 and 20 Ω from the ECLab software.

4. Conclusion

Formation of aggregates of Sq2 dye molecules on TiO_2 electrode was successfully suppressed by co-absorption of N719 dye molecules at the same time. Minimization of forming of aggregates of Sq2 dye molecules increases photo-performance of cells made from $TiO_2|(Sq2+N719)$ electrodes than compare to that of $TiO_2|Sq2$ and $TiO_2|N719$ electrodes.

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