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Enhancement of electrical and optical performance of N719 by co-sensitization

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ABSTRACT

This paper deals with the electrical, optical and electrochemical properties of a metal-free dye $C_{78}H_{74}O_8$ (AS-2), which has been used to improve the photo-detection properties of $C_{58}H_{86}N_8O_8RuS_2$ (N719) based Dye sensitized photo-sensors (DSPSs). Both dyes were mixed together in various proportions and the most promising ratio N719/AS-2 (1:0.25) was selected for staining photo-anodes for DSPS integration. The fabricated DSPSs were studied in terms of electrical parameters and photodetection properties. The N719/AS-2 (1:0.25) based DSPS were found to have a reduced leakage current, increased breakdown voltage and a closer proximity to an ideal diode, as compared to the N719 based DSPS. Further, the N719/AS-2 (1:0.25) based DSPS was also found to have better linearity at high irradiance levels, thus rendering the co-sensitized device useful as a photosensor in various applications. Electrochemical Impedance Spectroscopy (EIS) analysis was also performed to explain the interfacial charge recombination process.

1. Introduction

Dye sensitizer is one of the decisive parameters that determine the performance of a Dye-sensitized photosensor (DSPS). In a DSPS, the sensitizer (which are chemically bonded to the porous surface of the semiconductor) is responsible for capturing photons of incident light and transferring the resultant excited electrons to the conduction band of the semiconductor [1]. There are certain criteria that a dye molecule must fulfill to be used as a photosensitizer in a DSPS. An ideal sensitizer used in a single junction device should possess an optical absorption over a wide range of optical spectrum [2]. Further, it should also have attached groups for the firm coupling with the semiconductor oxide's surface. When excited (upon the absorption of a photon), the sensitizer should inject electrons into the solid semiconductor, with a quantum yield of unity. To minimize the losses during the electron transfer reaction the energy level of the sensitizer's excited state (LUMO) should be well matched to the lower edge of semiconductor's conduction band. When it comes to the redox potential, it should be high enough for the sensitizer to get regenerated/neutralized via electron donation from the redox electrolyte/hole conductor. Lastly, it should exhibit enough stability to withstand over years of exposure to light [3]. However, it is needed to bring improvements to the photodetection properties of DSPS to make them compete with the conventional technologies.

To fulfill the above-mentioned criteria, several types of dye molecules (containing diverse types of linking groups) have been developed and put to the test. Till today's date ruthenium-based metal complexes are the most commonly utilized sensitizers, owing to their wide absorption spectra and well matched HOMO and LUMO levels [4,5]. Other promising sensitizers include porphyrin and phthalocyanine systems, having strong absorption in the IR region, good thermal and chemical stability. These dyes use metal as central atom and have a low molar extinction coefficient leading towards weak light absorbance [6]. In addition, metal-free dyes based on coumarin, indoline, tetrahydroquinoline, triarylamine, and heteroanthracene, have also been employed [7]. Such dyes have higher molar extinction coefficient, are comparatively cheaper and environment friendly, however, they have narrow absorption spectra yielding efficiencies lower than that of metal-complex dyes. All the above-mentioned dyes (including the ones with the highest performance) have properties that are immensely inferior to that of an ideal dye and thus need to be optimized.

One of the key ways utilized for the optimization of the properties of a dye is called 'co-sensitization' in which an individual dye

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is mixed with other promising dye(s). It can provide an effective means of broadening the optical absorption range and in-turn increases the sensitivity of the DSPS, eventually resulting in an increased efficiency [8,9]. In addition, various other effects such as low charge transport resistance, longer electron lifetime, enhanced absorbance, broader IPEC, reduction in recombination kinetics, retardation of back reaction, depressed electron recombination, increased V_{oc}, might also be observed upon co-sensitization [10–12]. The current study, deals with improving the electrical and photo-detection properties of the fabricated DSPSs by means of co-sensitizing of Ru based N719 dye ($C_{58}H_{86}N_8O_8RuS_2$) with a newly developed organic dye named as AS-2 ($C_{78}H_{74}O_8$). Initially, absorption spectra for the dyes were measured. Later, the two dyes were mixed in different proportions and measured again for the absorption spectra. Upon, the selection of the right dye proportion, the TiO_2 based photo-anodes were soaked either in the N719 dye or dye cocktail solution. The DSPS involving a dye sensitized TiO_2 photo-anode and counter-electrode were fabricated and a comparison was established between the two dye-based photosensor, using a series of experiments for the extraction of (dark) electrical, photo-detection parameters.

2. Experimental

Fig. 1 shows the molecular structures of the N719 and AS-2 dyes. Initially, 0.5 mM solutions of AS-2 and N719 dyes were prepared in acetone, poured into a 1 ml cuvette and measured for their spectral absorbance within 300 nm to 950 nm wavelength range, using an optical spectrophotometer. Once optimized for their spectral absorbance, the optimized ratio was utilized for the sensitization of the TiO_2 semiconductor coated ITO photo-anodes. TiO_2 paste (Solaronix) was used to deposit a thin layer onto ITO substrates using doctor blade. The paste was allowed to dry in ambient environment for 30 min. Later, the films of TiO_2 were sintering at 450 °C, for a duration of 1 h. The thick of the TiO_2 films were 15 μm. The procedure applied for the preparation of the TiO_2 thin films was kept the same for all the samples. The photo-anodes were placed in a glass container (with the semiconductor layer facing upwards), and one of the numerous prepared dye solutions was poured over it, completely submerging the photo-anodes. The photo-anodes were allowed to sit in the container for 24 h. Then, the photo-anodes were taken out, rinsed with acetone and allowed to dry for 30 min, in the ambient environment. The photoelectrodes were sandwiched with an ITO/Pt-based counter-electrode, with the Meltonix sealant (Solaronix). The whole assembly was heated at 100 °C for the formation of an effective sealing. Later, high-performance HI-30 electrolyte was filled into the vacant space present between the two electrodes, using a drilled hole in the counter-electrode, Fig. 1 (b). The drilled hole was also sealed using sealant and a thin glass slab. The fabricated DSPS samples were later characterized for their electrical and photodetection properties, in light and dark conditions. To do so, Sunlite solar simulator (Abet Technologies) and Keithley 2400 SMU were utilized.

3. Results and discussion

3.1. Spectrophotometer absorbance

Initially, individual dyes (i.e., N719 and AS-2) were characterized for the spectral absorbance, using a spectrophotometer. As seen in Fig. 2, in case of N719 two major peaks occurred at 395 nm and 530 nm, indicating maximum absorbance of photons of light, while a minor peak occurred at 366 nm. For AS-2 dye, a major peak occurred around 550 nm and two minor peaks occurred at 510 nm and 390 nm. Since N719 is known for its high-power conversion efficiency, therefore, it was selected as the main dye, with AS-2 acting as a co-sensitizer. When co-sensitized with AS-2 in various proportions, significant changes to the absorbance plot were observed. Maximum overall absorbance of the dye cocktail solution was achieved when N719 was mixed with AS-2 in 1:0.25 (Fig. 2 inset). A total of three peaks were formed with the maxima of the highest peak occurring at 547 nm. The maxima of the other two peaks occurred at 510 nm and 391 nm. Since increased light absorbance results in an increased number of injected electrodes, eventually leading towards higher current density, therefore N719/AS-2 (1:0.25) dye cocktail was selected for semiconductor dye-sensitizing purposes, alongside N719. The cocktail yielding the optimized absorbance i.e. N719/AS-2 (1:0.25) presents the optimized absorption (balance between the AS-2 and N719), in the shorter wavelength region. Although the maximum absorbance achieved for co-sensitized dye solutions was less that N719, yet the

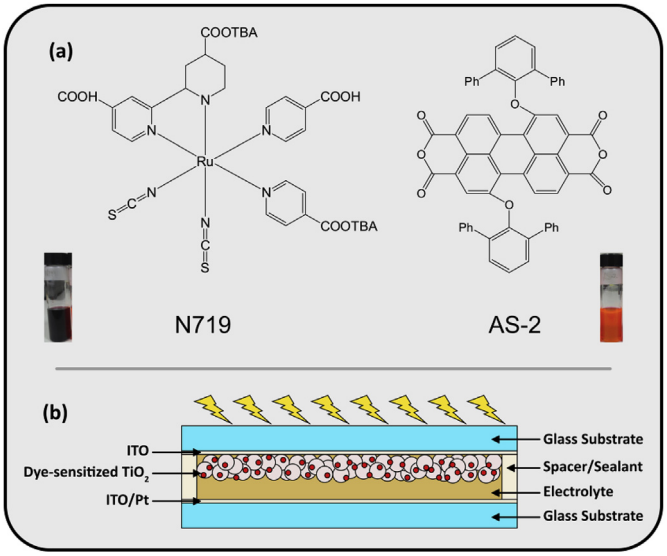

Fig. 1. (a) Molecular structures of N719 and AS-2, insets show original dye solutions contained in vials (b) configuration of the implemented DSPS devices.

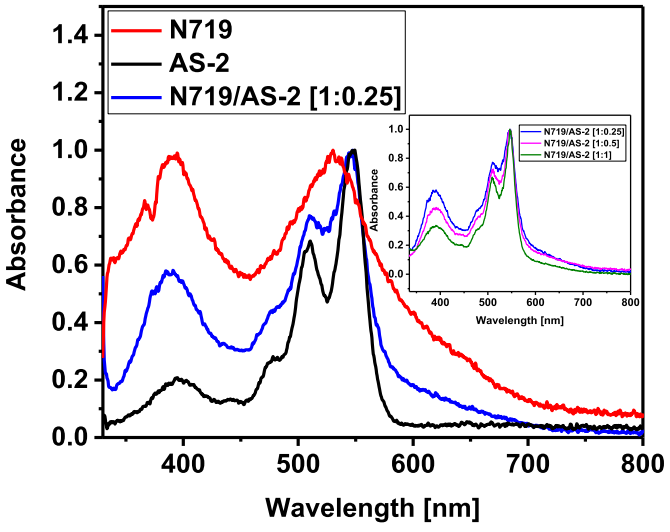

Fig. 2. Absorbance of individual and hybrid dyes with respect to wavelength, in UV/Vis region, inset: absorbance of dye cocktail solutions having various molar concentrations of N719 and AS-2 dye, plotted with respect to wavelength.