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Sensitization of TiO_2 and ZnO nanocrystalline films with acriflavine

M.K.I. Senevirathne [a], P.K.D.D.P. Pitigala [a], V. Sivakumar [a,c],
P.V.V. Jayaweera [a,b], A.G.U. Perera [a,b], K. Tennakone [a,b,*]

[a] *Institute of Fundamental Studies, Hantana, Kandy, Sri Lanka*
[b] *Department of Physics and Astronomy, Georgia State University, Atlanta, United States*
[c] *Department of Physics, University of Peradeniya, Peradeniya, Sri Lanka*

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Abstract

A comparison of acriflavine sensitized photoelectrochemical cells based on nanocrystalline films of TiO_2 and ZnO shows that the short-circuit photocurrent of the latter system is nearly an order of magnitude larger, despite the poor injection efficiency from this dye to ZnO. The above observation and disparity in dark currents in the two systems indicate that recombination of the injected carrier with acceptors in the electrolyte is faster in the TiO_2 cell sensitized with the same dye. A study of $1/f$ noise in the current through acriflavine and N3 dye coated nanocrystalline films of ZnO shows that that acriflavine is more strongly bonded to ZnO and not readily displaced by water molecules, which trap electrons and mediate recombination.

Keywords: Acriflavine; TiO_2; ZnO; $1/f$ noise

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1. Introduction

In recent years dye-sensitized solar cells have been optimized with improvement of the quality of the mesoporous TiO_2 film and synthesis of efficient sensitizers to match the solar spectrum [1–4]. Although dyes can be designed to obtain the appropriate optical absorption [5,6], ready prescriptions are not available for minimizing the recombination losses. Injection-geminate recombination kinetics for a given mesoporous oxide semiconductor substrate depends on the mode of anchoring of the sensitizer molecule to the oxide surface and its overall structure. It has also been observed that most sensitizers giving higher efficiencies in TiO_2-based dye-sensitized solar cells perform poorly when applied to those based on ZnO and SnO_2, the two other familiar stable metallic oxide semiconductors having similar band gaps and band positions [1]. There are also examples of dyes yielding higher energy and quantum conversion efficiencies when applied on ZnO or SnO_2, although the injection rates happen to be similar or even lower compared to that of TiO_2 [7–11]. It seems that bulk and surface properties of the semiconductor and also the mode of interaction of the dye with the oxide surface determine the extent of recombination (both geminate and non-geminate). In this note we present our observations on sensitization of nanocrystalline films of TiO_2 and ZnO with acriflavine (AC, i.e., 1,6diamino-10-methylacridinium chloride, the structural formula shown in Fig. 1a). Photoelectrochemical cells (PECs) with AC sensitized ZnO films showed higher short-circuit photocurrent and efficiency compared to the TiO_2 films sensitized with the same dye. Again dark current measurements of PECs made from AC coated films of these oxides, clearly indicate that the rate of recombination with acceptors is lesser for ZnO, in complete contrast to the behavior of same films sensitized with the N3 dye ([2,2′-bipyridyl 4,4′-dicarboxylate]Ru(II)).

The noise in the electric current through a semiconductor is highly sensitive to trapping and other interactions of carriers with defects and surface states [4–6]. A study of the noise power-spectrum of the current passing through the AC and N3 coated nanocrystalline films of ZnO suggests that AC bonds more strongly to ZnO compared to N3 and not readily desorbed

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[*] Corresponding author at: Institute of Fundamental Studies, Hantana, Kandy, Sri Lanka.
E-mail address: ktenna@yahoo.co.uk (K. Tennakone).

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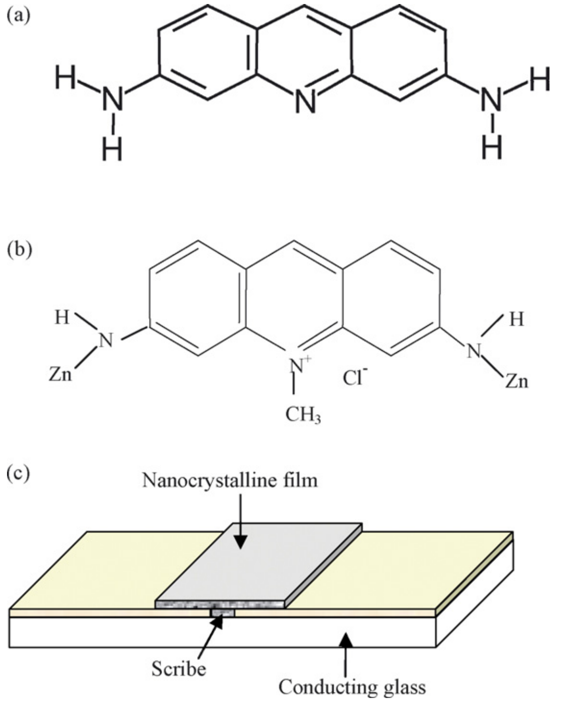

Fig. 1. (a) Structural formula of acriflavine, (b) the mode of acriflavine bonding to ZnO and (c) sample for measurement of 1/*f* noise in the current.

by moisture. Water molecules adsorbed on the ZnO and the TiO_2 surfaces traps electrons and act as recombination centers [7].

2. Experimental

Zinc oxide films were prepared by the method described below. Zinc oxide powder (10 g) is ground with few drops of acetic acid and the surfactant Triton X-100, adding sufficient ethanol to form a paste which is spread on fluorine-doped conducting tin oxide glass plates (1.5 cm × 1 cm, sheet resistance 12 Ω/sq) by doctor balding. The film was dried at 150 °C and thereafter sintering in air at 450 °C for 30 min. TiO_2 films were prepared by the same method using Degussa P25 TiO_2 powder. Films were coated with the dyes AC and N3 by soaking the plates in 0.40×10^{-3} M solutions of the dyes in ethanol. Photoelectrochemical cells (PECs) were made as usual by clamping the dyed film against a lightly platinized counterelectrode and filling the capillary space between the two plates with the electrolyte (0.6 M dimethylpropyl imidazolium iodide + 0.1 M LiI + 0.5 M *t*-butyl pyridine in methoxyacetonitrile). The amounts of dye adsorbed onto the films were estimated by measuring depletion of the dye in the coating solution spectrophotometrically. *I–V* characteristics of the cells were recorded using a source meter (Keithley 2420) and a calibrated power supply. Florescence emission spectra of AC aqueous solution and aqueous dispersions of AC adsorbed ZnO and TiO_2 were recorded using a Shimadzu RF-5000 Spectrofluorophotometer. The noise power intensity in the current through AC coated nanocrystalline films was measured by the procedure described previously using nanocrystalline films of TiO_2 and ZnO deposited on linear scribes (thickness ∼10 μm) drawn on conducting tin oxide glass (Fig. 1c). Measurement was conducted inside a thermostatic chamber provided with facilities for evacuation and purging of gases. Noise spectra (plot of noise power spectral density vs. frequency) were recorded using Stanford Research SR785 Fourier Transform Dynamic Signal Analyzer. FTIR spectra were recorded using NICOLET 6700 FT-IR spectrometer.

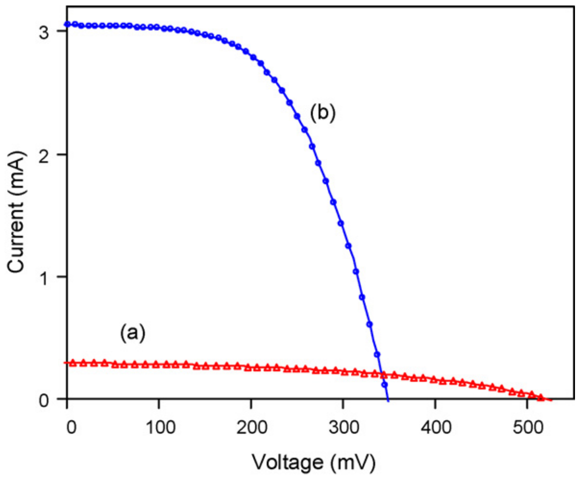

Fig. 2. *I–V* characteristics of acriflavine sensitized PECs made from (a) TiO_2 and (b) ZnO.

3. Results and discussion

The *I–V* characteristics of the cells at 1.5 AM, 1000 W m^{-2} illumination recorded using the source meter are shown in Fig. 2 and Table 1 summarizes the *I–V* parameters (I_{sc} = short-circuit photocurrent, V_{oc} = open-circuit voltage, FF = fill factor) of AC sensitized PECs made of TiO_2 and ZnO films (TiO_2/AC and ZnO/AC).

AC in solution has an absorption peak at 465 nm and a strong fluorescence emission at 484 nm. The fluorescence spectra (Shimadzu Spectrofluorometer RF-500) of suspensions of ZnO and TiO_2 containing the same amount of adsorbed AC are shown in Fig. 3. As electron injection quenches fluorescence, the lower fluorescence quantum yield in (Table 1) in ZnO/AC compared to TiO_2/AC, suggests a faster injection rate in the former system. Furthermore, the higher open-circuit voltage of the TiO_2/AC compared to the ZnO/AC, implies an enhanced rate of geminate recombination in the latter system (geminate recombination is the main factor that limits the open-circuit voltage to a value below the thermodynamic limit [1]). Despite above differences, the short-circuit photocurrent of ZnO/AC is seen to be nearly an order of magnitude higher than that of TiO_2/AC (Table 1). The

Table 1
I–V parameters of PECs made from acriflavine sensitized ZnO and TiO_2 films

Cell	I_{sc} (mA cm^{-2})	V_{oc} (mV)	FF (%)	Efficiency (%)
ZnO	3.048	346.8	55.63	0.588
TiO_2	0.296	515.6	45.42	0.069

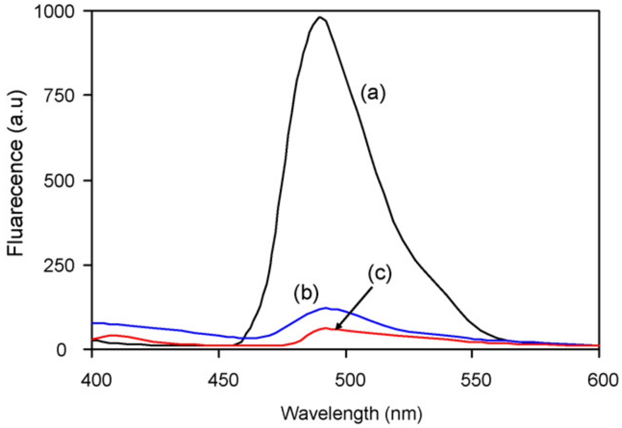

Fig. 3. Fluorescence spectrum of (a) an acriflavine aqueous solution, (b) a dispersion of acriflavine adsorbed ZnO and (c) a dispersion of acriflavine adsorbed TiO_2.

reason for this glaring difference between ZnO/AC and TiO_2/AC can be understood as faster recombination of carriers with acceptor states (i.e., I_3^- ions in the electrolyte) in the TiO_2-based cell.

We arrive at the same conclusion in examining the dark current [2] curves of the cells TiO_2/AC and ZnO/AC (Fig. 4a), the higher dark current in the former system at lower potentials indicates a faster combination of electrons with I_3^- at the interface between TiO_2/AC and the electrolyte compared to the ZnO/AC system. However, with the N3 dye the behavior of the dark current is just the opposite (Fig. 4b). Here, ZnO/N3 shows a higher dark current compared to TiO_2/N3 (Fig. 4b) suggestive of a higher recombination rate in the ZnO system.

Analysis of the noise in the electric current through nanocrystalline films of ZnO and TiO_2 sensitized by AC and N3 enables understanding the cause of the distinction between PECs made from these films. The current through bare TiO_2 and ZnO films housed in dry N_2 atmosphere exhibits signals of 1/*f* noise [3]. However, the noise is almost completely suppressed when the films are coated with AC (i.e., TiO_2/AC and ZnO/AC). The same behavior had been observed when N3 was coated on ZnO and TiO_2 films [3,4] (i.e., TiO_2/N3 and ZnO/N3). In nanocrystalline oxide films, trapping and detrapping and other interactions of electrons at the oxide surface generate 1/*f* noise [3]. The adsorbed dyes effectively passivate the trapping sites on the surface. In the nanocrystalline film the, trapping sites are either intrinsic defects on the surface or species adsorbed on the surface. Furthermore, surface defects are favorable sites for adsorption of foreign molecules and ions. The adsorbed dye passivates the defect structure and also prevents adsorption of species, which act as electron acceptors. Adsorbed electron acceptor species on the oxide surface generate 1/*f* noise in the electric current. When trace quantities of moisture (i.e., to raise the relative humidity ∼15%) is introduced into the chamber housing the films of ZnO/AC and ZnO/N3, 1/*f* noise begins to develop, but at a conspicuously faster rate and at a higher amplitude in ZnO/N3 (Fig. 5).

The bare TiO_2 and ZnO nanocrystalline films in N_2 also develop 1/*f* noise on introduction of moisture. Here, the intensity and the rate of development of 1/*f* noise happen to be exceedingly faster in ZnO films compared to TiO_2 films under same conditions. In contrast, the development of moisture-induced 1/*f* noise is greatly suppressed in ZnO/AC compared to that in TiO_2/N3 under the same conditions. Moisture seems to desorb N3 on ZnO much more readily compared to AC, because AC

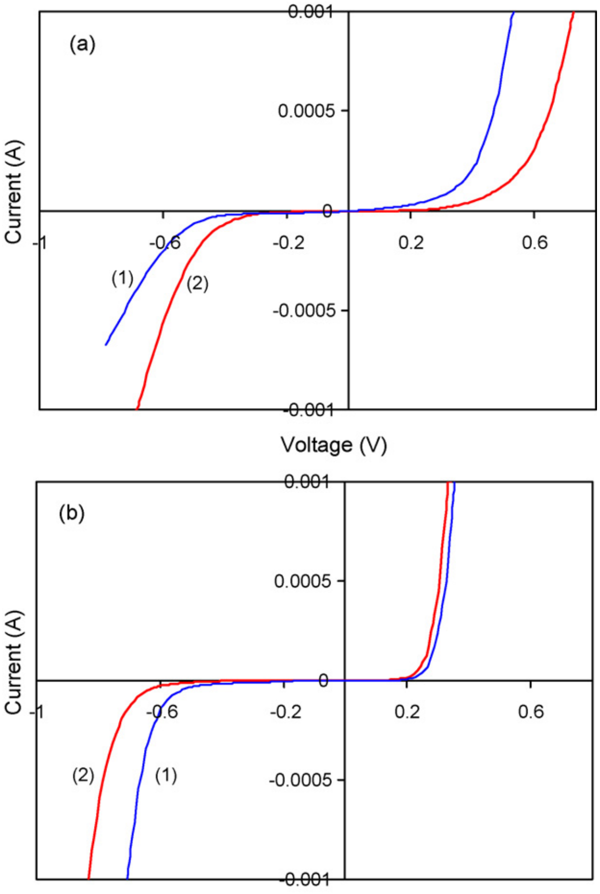

Fig. 4. Plot of dark current vs. voltage (a) acriflavine sensitized ZnO (curve 1) and TiO_2 (curve 2) and (b) N3 sensitized ZnO (curve 1) and TiO_2 (curve 2).

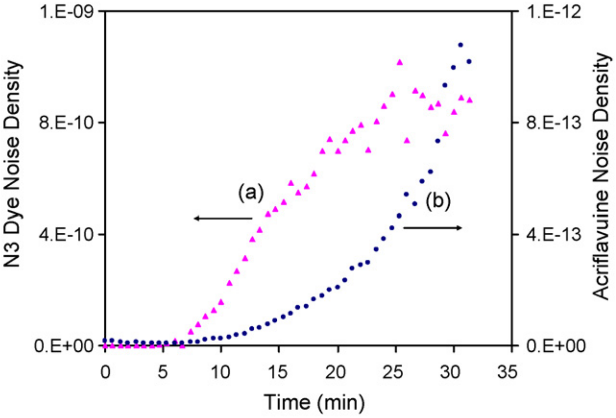

Fig. 5. Plot of the time development of the power spectral density (measured at 400 Hz) of noise in ZnO coated with N3 dye (curve a) and acriflavine (curve b) as moisture is introduced to the chamber housing the films.

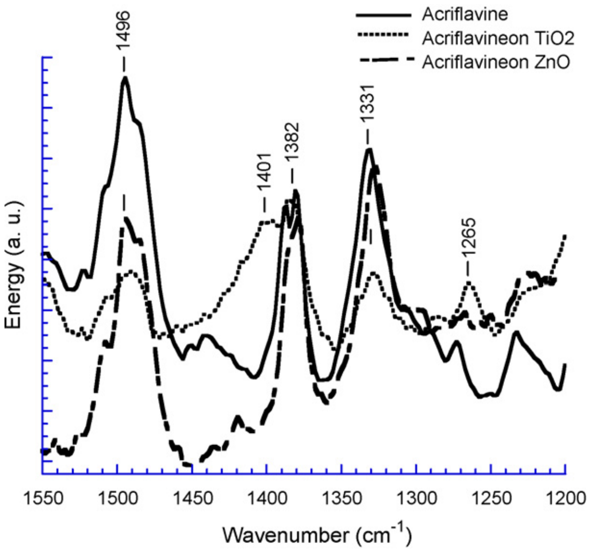

Fig. 6. FTIR diffuse reflectance spectra of acriflavine, acriflavine on ZnO and acriflavine on TiO_2.

bonds to ZnO more strongly than N3 and passivate it against interaction with moisture. At higher humidities the underlying cause for the observed effects may be more complicated as changes in the surface concentrations of the adsorbed dyes are more significant. The amine nitrogen in AC being basic has an affinity to strongly acidic sites on the ZnO surface. Generally both Lewis and Bronsted acid sites on an oxide surface bind organic compounds constituted of amino nitrogen. The FTIR spectra of AC and AC adsorbed on TiO_2 and ZnO presented in Fig. 6 shows that CN stretching of amine nitrogen at 1331 cm^{-1} is more conspicuously shifted in AC bonded to ZnO (AC bonds to TiO_2 and ZnO via amine N, Fig. 1b). This suggests that AC is bonded to Lewis acid sites on the oxide surface, as Bronsted acid sites would prefer attachment to heterocyclic nitrogen in AC.

It seems that trace quantities of water invariably present in the electrolyte bonds to the oxide surface desorbing some dye and acts as recombination centers. This effect is more prominent in TiO_2/AC as evidenced from the noise density, which are three orders of magnitude higher compared to ZnO/AC (Fig. 5). This explains why ZnO/AC cells have efficiencies well above TiO_2/AC. It is also possible that the sites absorbing moisture on these oxide surfaces act as recombination centers and in ZnO, AC passivates them more effectively.

4. Conclusion

The above investigation compares PECs made from nanocrystalline films of TiO_2 and ZnO sensitized with AC. The results indicate that the rate of recombination with acceptors at the surface is lesser in the latter system. AC in ZnO is not readily desorbed and replaced by water molecules, which act as trapping site for electrons, and concurrently AC may also be passivating the trapping sites on the ZnO surface. The behavior is different to that of the N3 and many other dyes, which give the highest efficiency when the sensitizing substrate is TiO_2. Results indicate that the mode of bonding of a dye to the semiconductor surface influences not only the rate of electron injection and geminate recombination but also the recombination of electrons with acceptors in the electrolyte, during their transit to the back contact. Adsorbed moisture on the oxide surface acts as recombination centers and a stronger bonding of the dye prevent its desorption and replacement by moisture.

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