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A high efficiency indoline-sensitized solar cell based on a nanocrystalline TiO₂ surface doped with copper

T R C K Wijayarathna¹, G M L P Aponsu¹, Y P Y P Ariyasinghe¹, E V A Premalal¹, G K R Kumara² and K Tennakone¹

 ¹ Institute of Fundamental Studies, Hantana, Kandy, Sri Lanka
² Department of Fundamental Studies, SPD Laboratory, Shizuoka University, Hamamatsu, Japan

E-mail: tenna@ifs.ac.lk

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Abstract

Dye-sensitized photoelectrochemical solar cells made from nanocrystalline films of TiO_2 doped with copper and sensitized with indoline 149 dye are found to have impressively higher efficiencies compared to equivalent cells made from undoped films. The surface concentration of copper atoms on the TiO_2 where this effect is optimized is nearly the same as the concentration of dye molecules on the TiO_2 surface. Copper doping shifts the flat-band potential of TiO_2 in the negative direction, which is favorable for increasing the open-circuit voltage of the cell. It is suggested that in addition to the linkage of the carboxylate ligand of the dye to the TiO_2 surface. The coordination of the dye to copper seems to have a positive influence on the efficiency of the cell.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The discovery of the concept of a dye-sensitized photoelectrochemical solar cell based on nanocrystalline oxide semiconductors more than two decades ago continues to receive wide attention as a cheaper alternative to conventional photovoltaics [1, 2]. Basically, the mechanism of operation of these devices depends on the absorption of light by a pigment anchored to a nanocrystalline high band-gap n-type oxide semiconductor, following injection of electrons to the semiconductor by the excited dye molecules. The positive charge on the dye cation scavenged by a donor species in the electrolyte is diffusively transported to a counter-electrode. The energy conversion efficiency achievable depends on many factors: (1) the bulk properties of the semiconductor (i.e., bandgap, band positions, conduction band density of states) and the structure of the film (i.e., crystallite size, porosity, roughness factor), (2) the photophysical properties of the dye (i.e., LUMO and HOMO positions, extinction coefficient) and the mode of anchoring of the dye molecules to the semiconductor surface, (3) the nature of the redox electrolyte and electrocatalytic

properties of the counter-electrode. Significant improvements have been made in structuring the nanocrystalline films, synthesis of superior sensitizers and redox electrolytes, and fabrication techniques [3]. An important recent development is the identification of metal-free organic dyes capable of delivering energy conversion efficiencies approaching that of the best Ru-bipyridyl dyes [4–9]. In this context high extinction coefficient indoline dyes are quite promising because of their good stability [4, 5], low cost, and ease of synthetic procedures. We have found that the efficiencies of dyesensitized solar cells based on indoline 149 can be further enhanced by surface doping of TiO_2 with copper. Evidence is presented showing that copper doping increases the opencircuit voltage and suppresses recombination of the injected electron with acceptors in the electrolyte.

2. Experimental details

In order to obtain reproducible results and easy comparison, a simple procedure was used to prepare TiO_2 films. A mixture



Figure 1. Variation of the efficiency of the cell (1000 W m^{-2} , 1.5 AM illumination) with the surface concentration of copper atoms on the TiO₂ surface.

of TiO₂ powder (Degussa P25, 200 mg, median particle size 30 nm), 95% ethanol (2 ml), glacial acetic acid (10 drops) and Triton X-100 (1 drop) was ground to form a thick paste. The paste was doctor bladed onto fluorine doped conducting tin oxide (FTO) glass plates (sheet resistance 15 Ω sq⁻¹, 0.5×1.5 cm², active area 0.25 cm²) and heated in air at 550 °C for 30 min. Copper doped TiO₂ films were prepared by the same method after incorporating a measured volume of 0.025 M CuCl₂ in ethanol to the mixture used for preparation of the paste. Both types of film used for fabricating cells had a thickness of $\sim 10 \ \mu m$. The surface concentration of Cu atoms in the films was calculated from the knowledge of Cu incorporated into a known weight of TiO₂. After sintering, the plates were washed with water to remove any unreacted CuCl₂ and again sintered at 550 °C for 5 min. The specific surface area of the sample films were estimated by determining the amount of the N3 dye adsorbed after depletion of the dye into alcoholic alkaline solution and spectroscopic estimation. To determine the exact amount of copper in the film, the water used for rinsing the plates was tested for copper by atomic absorption spectroscopy. Indoline 149 was coated on the TiO₂ surface by soaking the plates in the dye solution $(1.5 \times 10^{-4} \text{ M in } t$ -butyl alcohol + acetonitrile, 1:1 by volume) for 2 h. The amount of dye adsorbed was estimated by measuring the depletion of the dye in the coating solution spectrophotometrically. Photoelectrochemical cells were fabricated by clamping a platinum sputtered FTO glass plate onto the dyed surface and filling the capillary space with the electrolyte (0.5 M tetrapropyl ammonium iodide + 0.05 M iodine in 1:4 by volume mixture of acetonitrile + ethylene carbonate). I-V characteristics of the cells at 1000 W m⁻² 1.5 AM simulated sunlight were recorded using a Keithley sourcemeter. The simulator lamp was calibrated using a silicon diode to set the light intensity at 1000 W m⁻². The Mott– Schottky plots of TiO₂ and copper doped TiO₂ films in 0.1 M Na₂SO₄ were recorded using a Hewlett-Packard 4276A LCZ meter, and an HJ Instruments potentiostat recorded the dark

Table 1. I-V parameters (I_{sc} = short-circuit photocurrent, V_{oc} = open-circuit voltage, η = efficiency, FF = fill factor) of different systems sensitized with indoline 149. (a) Undoped TiO₂ in the electrolyte without 4-*tert*-butylpyridine; (b) TiO₂ optimally doped with Cu in the electrolyte without 4-*tert*-butylpyridine; (c) undoped TiO₂ in the electrolyte with 4-*tert*-butylpyridine; (d) TiO₂ optimally doped with Cu in the electrolyte with 4-*tert*-butylpyridine; (e) TiO₂ sensitized with indoline 149 complexed with Cu²⁺ in the electrolyte with 4-*tert*-butylpyridine; 149 in the electrolyte with 4-*tert*-butylpyridine; 149 in the electrolyte with 4-*tert*-butylpyridine.

Cell configuration	$I_{\rm sc}~({\rm mA~cm^{-2}})$	$V_{\rm oc}~({\rm mV})$	FF (%)	η (%)
a	11.9	777.8	62.4	5.8
b	14.8	833.7	65.6	8.1
с	11.2	857.8	64.5	6.2
d	10.3	833.8	67.9	5.8
e	5.2	573.7	61.1	1.8
f	4.9	747.8	65.3	2.4

I-V curves. A He–Ne laser and mechanical shutter were used to record the photovoltage transients using an oscilloscope.

3. Results and discussion

During the sintering process, copper gets deposited on the TiO_2 surface via the reaction

$$2x\operatorname{CuCl}_2 + \operatorname{O}_2 \to 2\operatorname{Cu}_x\operatorname{O} + 2x\operatorname{Cl}_2. \tag{1}$$

As sintering is at a relatively low temperature for a short duration, the Cu dopes on the TiO₂ crystallite surface. Nevertheless, the Cu remains firmly bonded to the TiO₂ surface and its removal requires prolonged warming with strong HNO₃. On increasing the sintering temperature or prolonging the sintering at 550 °C, the efficiency falls below that of cells made from bare TiO₂ films subjected to similar variations. This suggests that the diffusion of the dopant into the bulk of the crystallites is detrimental. At the level doping used in the experiments, the UV-visible diffuse reflectance spectra did not indicate any features significantly different from those from the undoped films, indicating that the doping has no major effect on the band-gap. When indoline 149 is used as the sensitizer, the efficiency of the cell gradually increases above that of bare TiO₂ as the surface concentration of Cu (S_{Cu}) is increased, reaching an optimum when $S_{\rm Cu} = 1.67 \times 10^{14} \, {\rm cm}^{-2}$ (figure 1). At much higher values of S_{Cu} , the efficiency goes well below that of the cells made of bare TiO_2 . The I-Vcharacteristics of indoline-sensitized cells with undoped and Cu doped TiO_2 films are shown in figure 2. Table 1 gives the I-V parameters (I_{sc} = short-circuit photocurrent, V_{oc} = opencircuit voltage, η = efficiency, FF = fill factor) of the cells. At the optimum S_{Cu} , the efficiency of the doped cell reaches 8.1% compared to 5.8% for an equivalent cell with an undoped TiO₂ film. It is seen that Cu doping enhances other I-Vparameters as well (table 1). The photocurrent action spectrum of the Cu doped cell presented in figure 3 corresponds to a peak (581 nm) incident photon to photocurrent conversion efficiency (IPCE) of 82%. In the undoped system, the peak point in the photocurrent action spectrum is red-shifted by ~68 nm with an IPCE of 78%. It is interesting to note that the effect of Cu



Figure 2. I-V characteristics of indoline 149 sensitized cells constituted of (a) undoped TiO₂ in the electrolyte without 4-*tert*-butylpyridine; (b) TiO₂ optimally doped with Cu in the electrolyte without 4-*tert*-butylpyridine; (c) undoped TiO₂ in the electrolyte with 4-*tert*-butylpyridine; (d) TiO₂ optimally doped with Cu in the electrolyte with 4-*tert*-butylpyridine; (e) TiO₂ sensitized with indoline 149 complexed with Cu²⁺ in the electrolyte without 4-*tert*-butylpyridine and (f) TiO₂ sensitized with indoline 149 in the electrolyte with 4-*tert*-butylpyridine.



Figure 3. Photocurrent action spectrum of the indoline 149 sensitized cell with (a) Cu doped TiO₂ and (b) undoped TiO₂.

doping disappears on incorporation of 4-*tert*-butylpyridine to the electrolyte, in complete contrast to the behavior of cells made of undoped TiO₂ (table 1). A comparison of dark I-Vcharacteristics (figure 4) of the indoline-sensitized cells based on Cu doped (at optimum S_{Cu}) and bare TiO₂ films shows that current onset under reversed bias occurs at ~0.60 and 0.10 V in the two systems. On incorporating 4-*tert*-butylpyridine into the electrolyte, the opposite behavior was observed; here the onset under reversed bias occurred at a higher voltage in the cells with undoped TiO₂ films. The above difference in dark I-V characteristics of the doped and undoped cells is a clear indication that the recombination is better suppressed in the



Figure 4. Dark I-V characteristics of (a) a Cu doped cell and (b) an undoped cell in an electrolyte without 4-*tert*-butylpyridine.



Figure 5. Photovoltage transients of the cells with TiO_2 films (a) doped with Cu and (b) undoped.

former cell. The photovoltage transients of the two cells shown in figure 5 confirm this. The exceedingly fast decay of the photovoltage of the doped cell compared to the undoped cell implies that doping effectively suppresses the recombination loss. The fast decay indicates a decrease in the carrier trapping rate, one of the main causes of recombination.

The Mott–Schottky plots for TiO_2 and Cu doped TiO_2 (doping level = S_{Cu}) shown in figure 6 indicate that the doping shifts the flat-band potential (FB) of the latter film in the negative direction by 0.17 V. When the doping concentration is increased beyond S_{Cu} , the FB becomes more negative.

The above observations can be understood on the basis of the following hypothesis. An even distribution of Cu atoms on the TiO₂ surface is assumed. The average distance between the Cu atoms ($\sim [S_{Cu}]^{-1/2}$) is ~ 0.8 nm, a distance that is of the same order of magnitude as the linear dimension of the indoline 149 dye molecule. Alternatively, the dye surface concentration (S_{dye}) is same order of magnitude as S_{Cu} (the measured value of the amount of dye on the film is 9.3×10^{16} molecules cm⁻²; a roughness factor of ~ 840 yields $S_{dye} \sim 1 \times 10^{14}$ cm⁻²).



Figure 6. Mott–Schottky plots for (a) TiO_2 and (b) Cu doped TiO_2 (supporting electrolyte 0.1 M Na₂SO₄).

Thus at the optimum, each dye molecule is associated with one copper atom, indicating an interaction between copper and the dye. Indoline 149 anchors to the TiO2 surface via the carboxylate moiety. The Fourier transform infrared (FTIR) signals originating from the carboxylate ligand in indoline coated TiO₂ and copper doped TiO₂ are identical, suggesting that, in both cases, the carboxylate binds to TiO_2 . Sulfur in the rhodanine rings of indoline 149 could coordinate with copper, and a schematic diagram indicating a possible mode of bonding of indoline 149 to Cu atoms on the surface of TiO_2 is shown in figure 7. The distinctive differences in the photocurrent action spectrum of the doped cell compared to the undoped cell (figure 3) is a clear indication of an interaction of indoline with copper atoms on the TiO₂ surface. In addition to the blue-shift of the peak position in the doped cell, there are other distinct differences in the two spectra. The sharp peak at 510 nm in the undoped cell is smoothed out in the doped cell and its profile is narrower. The distinction of the two spectra also supports the assumption that copper atoms reside on the TiO_2 surface, permitting interaction with the dye. When Cu^{2+} ions are introduced to an indoline 149 solution, the Cu complexes with the dye, which is accompanied by a color change. In the absorption spectra of alcoholic solutions of indoline 149 and the same complexed with copper, the absorption peaks are located at 515 and 521 nm respectively. The complexed dye adsorbs well onto TiO₂, but the efficiency is drastically reduced (table 1). Obviously, the complexed dye would not coordinate with Cu on the TiO₂ surface. Possibly, the photo-induced electron delocalization pattern in the dye molecule also undergoes a change on coordination of rhodanine rings with Cu. Interaction of the dye with Cu could also suppress aggregation of the dye molecules as suggested by the blue-shift of the absorption peak of the doped cell. If the electron is driven towards the metal (Cu), the injection rate to TiO_2 via the carboxylate linkage will be reduced. A natural question that arises is about the most probable point of injection of the electron to TiO₂ (i.e., carboxylate ligand attached to TiO₂ or coordination of a rhodanine ring moiety to a Cu atom). Although there is no experimental evidence, an involvement of the coordination of rhodanine to Cu atoms



Figure 7. Schematic diagram suggesting the mode of interaction of indoline 149 with the TiO₂ surface.

(attached to TiO_2) may have important implications on electron injection and geminate recombination kinetics. Indoline 149 forms non-quenching J-aggregates on the TiO₂ surface [5]. The broadening of the action spectrum of the indoline 149 sensitized cells and the extension of the responsivity towards the red region result from this effect. It is natural to expect that when this dye is bonded to both Cu atoms and TiO₂ (figure 7), the aggregation is circumvented. The narrower profile of the action spectrum of the doped cell compared to the undoped cell seems to originate from the prevention of aggregation in the former system.

Many factors seem to be responsible for the dramatic improvement of efficiency of the cell on Cu doping of TiO₂. The shift of the flat-band potential of TiO₂ in the negative direction increases the open-circuit voltage, as observed. The higher dark current onset potential of the Cu doped cell compared to the undoped cell indicates that the recombination probability of the injected electron with acceptors in the electrolyte is less in the former system. Figures 8(i) and (ii) shows the variation of the energy conversion efficiency and the open-circuit voltage of the two cells with the intensity of illumination. In the undoped cell, the efficiency decreases faster with the increase of the light intensity compared to the doped cell. In the doped cell, the open-circuit voltage remain nearly constant at higher μ intensities (i.e., >900 W m⁻²), whereas in the undoped cell a saturation voltage is not approached even at very high intensities. The pumping of electrons into TiO₂ via sensitized injection raises the quasi-Fermi level (QFL), the height of which determines the opencircuit voltage. Recombinations limit the build-up of the QFL. The results further confirm that copper doping suppresses recombination, enabling upward lift of the QFL even at lower light intensities when the electron pumping rate is slow.



Figure 8. Variation of (i) efficiency and (ii) open-circuit voltage of (a) Cu doped and (b) undoped cells with the light intensity.

Despite the significantly higher efficiency of the doped cell compared to the undoped cell, the peak IPCEs of the two cells are of the same order of magnitude. The IPCEs are measured at very low intensities (\sim 50 μ W cm⁻²) where the recombination losses are less pronounced. Copper doping of TiO₂ resembles the effect of 4-*tert*-butylpyridine, the adsorption of which shifts the flat-band potential in the negative direction and suppresses recombination, increasing the open-circuit voltage. 4-*tert*butylpyridine [10–12] is believed to passivate intra-band-gap defects in TiO₂ which act as recombination centers [13]. Presumably, the copper atoms are also attached to defect sites on TiO₂.

When Cu doped and undoped films are sensitized with the N3 dye, the efficiency and other I-V parameters of the doped cell decrease, in complete contrast to the behavior with indoline 149. Clearly, the interaction of indoline and Cu also plays a crucial role in enhancing the efficiency. The mechanism involved is not fully understood. Perhaps, the firm bonding of the indoline 149 molecule to the TiO₂ surface at two points (i.e., carboxylate link to TiO₂ and coordination of sulfur in the rhodanine rings to Cu atoms as in figure 6) covers the TiO₂ surface without leaving any voids. Recombinations occur at the voids where the electrolyte is in direct contact with the TiO_2 surface. The observation that 4-*tert*-butylpyridine in the electrolyte interferes with the beneficial effect of Cu doping can be understood. The stronger bonding of 4-*tert*-butylpyridine to Cu could yield the linkage of the indoline 149 molecule to Cu. This happens if Cu atoms are located on the TiO_2 surface.

4. Conclusion

The efficiency of indoline 149 sensitized photoelectrochemical solar cells increases significantly when the nanocrystalline TiO₂ is surface doped with Cu to a concentration similar to the dye concentration. The prescription adopted to prepare TiO₂ films in this investigation is not optimized standard procedure. However, the efficiency increased from 5.8 to 8.1% on doping the TiO_2 film with Cu. We believe that the efficiency can be further improved by optimization of the TiO₂ film casting procedure. Preliminary experiments indicate that the copper doped cell is as stable as the undoped cell. There is no evidence that Cu leaches into the electrolyte. Possibly, the coordination of the dye to the copper adds to the chemical stability of the copper bonded to the TiO₂ surface and also suppress the aggregation of the dye molecules. The exact mode of coordination of the dye to copper sites in the TiO₂ surface is not clear. As the surface concentration of Cu on TiO₂ is very low, the resolution of the FTIR measurements is not sufficient to obtain any clues as to the mode coordination of indoline 149 dye to the copper doped TiO₂ surface. The involvement of both sulfur and nitrogen in the rhodanine rings is not ruled out. The present investigation suggests that surface modification of TiO₂ and the incorporation of suitable accessory ligands to the dye molecule are promising strategies to enhance the efficiencies of dye-sensitized solar cells. Although conclusive evidence is not available to single out one mechanism, the increase in efficiency and the behavior of photocurrent transients suggest that Cu doping suppresses recombination.

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