

## EFFECTS OF NI DOPING OF THE NANOSTRUCTURED PHOTO ANODE ON THE PERFORMANCE OF DYE SENSITIZED SOLAR CELLS

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### INTRODUCTION

Since the first report of high energy conversion efficiency for dye-sensitized solar cells (DSSCs) in 1991, there has been intense interest in understanding the parameters that control cell operation and performances. Even though, energy conversion efficiencies of about 11% (AM 1.5 solar irradiation) have been reported for regenerative DSSCs based on nanocrystalline TiO<sub>2</sub> films sensitized with ruthenium dye (N3) using triiodide/iodide in an organic solvents, most DSSCs still deliver short circuit current densities and open circuit voltages much less than the theoretical maximum values, resulting in lower photo conversion efficiencies. This lower performances can be attributed with many factors, including the degradation and desorption of the dye, leakage of the liquid electrolyte, corrosion of the Pt counter electrode by the iodide/triiodide redox couple in the electrolyte and poor semiconductor film morphology that leads to fast recombination process between the injected electrons and the oxidized species in the electrolyte. Many efforts have been made to rectify above problems but very little has been done to alter the semiconductor electrode film structures use in these DSSCs. It is observed that metal ion doping (by both acceptor or donor type elements) can significantly modify these structure properties (Gratzel 2001). Therefore, in recent years, an intense effort has been focused on the preparation of metal oxide nanocrystals either doping with metal ions or coated with another oxide material owing to their suitability in use of DSSCs. In this context, our research group has already attempted to improve the efficiency by doping some metal nano-particles with TiO<sub>2</sub> (Wijayarathna *et al* 2008). As a continuation, in the present work, we investigated the effect of Ni doping in the semiconductor electrode on the performance of DSSCs which gives much insight into the mechanisms of band positions and trap levels. We suggest that the mechanism of charge transport process of the DSSCs based on Ni doped nanocrystalline TiO<sub>2</sub> films with the evidences for trap-filling conditions, band positions and changes in the band gap.

### METHODOLOGY

In order to obtain reproducible results and easy comparison, a simple procedure was used to prepare TiO<sub>2</sub> films. A mixture of TiO<sub>2</sub> powder (Degussa P25, 200 mg, median particle size 30 nm), 95% ethanol (2 ml), glacial acetic acid (10 drops) and Triton X-100 (one 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 ohm/sq, 0.5 x 1.5 cm<sup>2</sup>, active area 0.25 cm<sup>2</sup>) and heated in air at 550° C for 30 min. Ni doped TiO<sub>2</sub> films were prepared by the same method after incorporating a measured volume of 0.05 M NiCl<sub>2</sub> in ethanol to the mixture used for preparation of the paste. Both types of films used for fabricating cells had a thickness of ~ 10 μm and the ratio of Ni in the films were calculated from a knowledge of the Ni incorporated into a known weight of TiO<sub>2</sub>. After sintering, plates were washed with water to remove any un-reacted NiCl<sub>2</sub> and again sintered at 550° C for 5 min. To determine the exact amount of Nickel in the film, the water used for rinsing the plates was tested for Nickel by atomic absorption spectroscopy. Indoline 149

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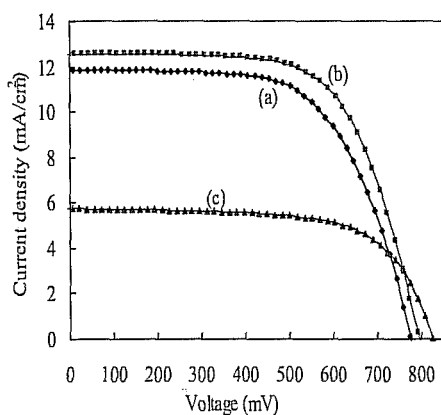
was coated on  $\text{TiO}_2$  surface by soaking plates in the dye-solution ( $1.5 \times 10^{-4}$  M in *t*-butyl alcohol with acetonitrile, 1:1 by volume) for 2 hrs. DSSCs were fabricated by sandwiching and clamping a platinum sputtered FTO glass plate with the dye adsorbed  $\text{TiO}_2$  electrode and filling the capillary space with the electrolyte (0.5 M tetrapropyl ammonium iodide with 0.05 M iodine in 1:4 by volume mixture of acetonitrile + ethylene carbonate). Current-voltage (J-V) characteristics of the cells at  $100 \text{ mW cm}^{-2}$  (AM 1.5) were measured using a home assembled and calibrated solar simulator consisting of a Keithly 2000 multimeter and a computer controlled HA-301 Potentiostat. A Xenon 500 lamp was used with AM 1.5 filters to obtain the simulated sunlight with the intensity of  $100 \text{ mW cm}^{-2}$ . The intensity of the light was calibrated using an ILT 1700 Research radiometer. The Mott-Schottky plots of  $\text{TiO}_2$  and Ni doped  $\text{TiO}_2$  films in 0.5 M  $\text{Na}_2\text{SO}_4$  were recorded using a Hewlett Packard 4276A LCZ meter. UV-Visible absorption spectra were obtained by Shimadzu UV-2450 UV-Vis spectrophotometer while the action spectra (Incident to photon to current conversion efficiency (IPCE)) of the solar cells were obtained using a Nikon Monocromater-Auto scanner A-C-101 coupled to a computer via a Keithly 2000 multimeter.

## RESULTS AND DISCUSSION

During the sintering process, Ni gets deposited as NiO with the  $\text{TiO}_2$  crystallites and the colour of the Ni doped  $\text{TiO}_2$  is pale yellow. However, the contrast of the color varies on the mole ratios of  $\text{TiO}_2$  and Ni (1:*r*). When the amount of Ni is increased (*r*) both the photo current density ( $J_{\text{SC}}$ ) and the photo voltage ( $V_{\text{OC}}$ ) increase. Out of the various compositions studied, the best composition prepared with the  $r = r_n = 0.44448 \times 10^{-3}$  gives the maximum value of the  $J_{\text{SC}}$  and therefore the highest efficiency of the DSSCs fabricated with indoline 149 dye. However, further increase of *r*, resulted in decreases of the  $J_{\text{SC}}$  while increases the  $V_{\text{OC}}$  up to  $r = r_v = 5.77824 \times 10^{-3}$  and at much higher values than that of  $r_v$ , both the  $V_{\text{OC}}$  and  $J_{\text{SC}}$  decrease to the values well below the values obtained for the cells based on bare  $\text{TiO}_2$ .

Figure 1 shows the current-voltage (J-V) characteristics obtained from the cells fabricated by sandwiching with  $\text{TiO}_2$  electrodes having different Ni compositions and the important cell parameters extracted from figure 1 is tabulated in table 1.

As it can be seen from the figure and the table, DSSCs prepared with undoped  $\text{TiO}_2$  delivered a



$J_{\text{SC}}$  of  $11.9 \text{ mA cm}^{-2}$ , with an efficiency of 5.8%. The solar cells with Ni ( $r = r_n$ ) doped delivered  $J_{\text{SC}}$   $12.5 \text{ mA cm}^{-2}$  with an efficiency of 6.5% (average of 5 samples). The addition of Ni to the semiconducting  $\text{TiO}_2$  composite enhances all the solar cells parameters including the filling factor as shown in the table. The open circuit photo voltage of the Ni doped cell reaches  $\sim 838 \text{ mV}$  with higher composition of Ni ( $r_v = 5.77824 \times 10^{-3}$ ) while decreasing the photo current to very low value as indicated in figure 1. One of the reasons for this decline might be due to the in cooperation between dye molecules with Ni and baffle electron leakage from dye molecule to  $\text{TiO}_2$  surface.

Figure 1. Electrical characteristics of indoline 149 sensitized cells constituted of the cell based on (a) Undoped  $\text{TiO}_2$  film (b) Ni ( $r = r_n$ ) doped  $\text{TiO}_2$  film and (c) Ni ( $r = r_v$ ) doped  $\text{TiO}_2$  film.

The band gap values estimated from the UV-visible diffuse reflectance spectra for both doped and undoped films and found that the addition of Ni to the TiO<sub>2</sub> effect on the reduction of the band gap. Mott-schottky plots for bare TiO<sub>2</sub> and Ni doped TiO<sub>2</sub> (for  $r = r_n$  and  $r = r_v$ ) are shown in figure 2. This indicates that the doping of Ni, shifts the potential of conduction-band (CB) in negative direction by  $\sim 0.35$  eV and when the doping ratio is further increased to  $r = r_m$ , and at further doping, CB moves to more negative side ( $-3.8$  eV at  $r = r_v$ ) with respect to the vacuum scale.

Table 1: Electrical parameters of indoline 149 sensitized cells constituted of the cell based on (a) Undoped TiO<sub>2</sub> film (b) Ni ( $r = r_n$ ) doped TiO<sub>2</sub> film.

Cell configuration	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF	$\eta\%$
(a)	777.8	11.9	62.4	5.8
(b)	794.5	12.5	65.3	6.5

indicates that the carrier trapping rate is higher in the undoped cells than the doped cells. Therefore, injected electron from the dye molecules on the conduction band of the bare TiO<sub>2</sub> anode can fall into unoccupied trap states, which is one of the main path for recombination (Wu *et al* 2010).

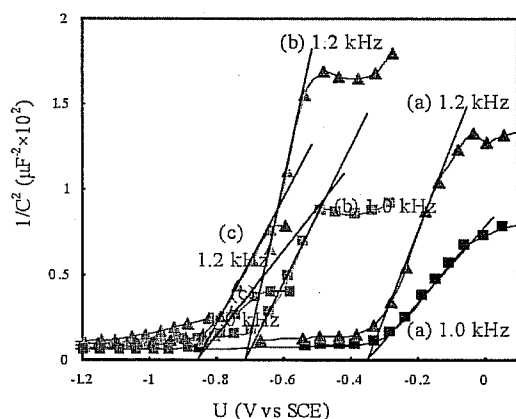


Figure 2 . Mott-Schottky plots for (a) bare TiO<sub>2</sub>, (b) Ni doped ( $r=r_n$ ) TiO<sub>2</sub> (c) Ni ( $r = r_v$ ) doped TiO<sub>2</sub> at different frequencies.

and hence the decline of the band gap implies that the Fermi level (FL) of the composite film goes above the value, that for the bare TiO<sub>2</sub> film (figure 3) which is responsible for the increase in photo voltage, because the difference between Fermi level and the Nernst potential of the redox level determine the photovoltage. On the other hand, it was also observed that, no shift in the peak positions of the incident photon to current efficiency (IPCE) values for the devices with doped and undoped TiO<sub>2</sub> films, strongly suggesting that the bonding of dye molecules with Ni do not affects the performances of the photo current significantly. The calculated dye surface concentrations for the Ni ( $r = r_n$ ) doped and undoped TiO<sub>2</sub> films were found to be in the same order of magnitude ( $9.35 \times 10^6$  molecules cm<sup>-2</sup>) indicating that the enhancement in the cell performances is not due to the amount of the dye molecules adsorbed to the TiO<sub>2</sub> surface.

In nano-particulated TiO<sub>2</sub> system, electron transportation is strongly affected by trapping and de-trapping events. The photo voltage transient studies for both cells showed that an extremely slow decay of the photo voltage of the undoped cells. Which

Among the many factors responsible for this enhancement in the photo cell efficiency, one of the most possible factors is the trap hole filling by the doping of Ni and thereby avoiding the recombination process through the trap levels as illustrate in the figure 3 (a,b) (Wu *et al* 2010). However, NiO is a *p*-type semiconductor having band gap of  $\sim 4$  eV, with CB and VB position at  $\sim -1.8$  eV and at  $\sim -5.4$  eV (wrt vacuum scale) respectively (Gratzel 2001, Simmons *et al* 1971, Mora-Sero and Bisquet 2003, Murphy 2007). The *p*-type nature of the NiO is confirmed from the Mott-schottky analysis and, it was also observed that, doping of Ni shifts the CB potential to the negative side, and thereby increases the CB potential of Ni doped TiO<sub>2</sub> film. Shifting of the CB position

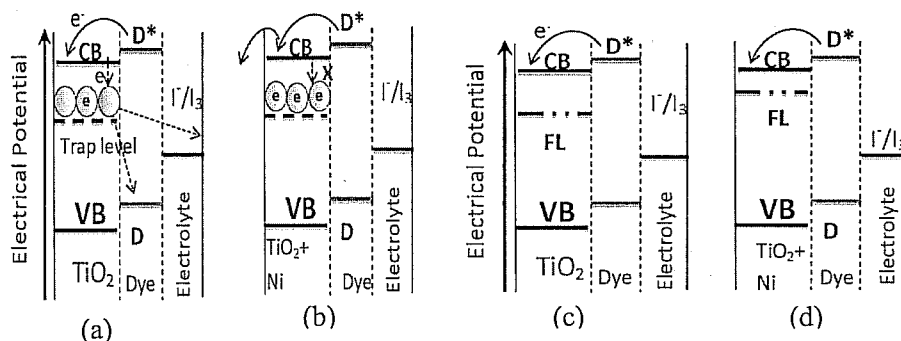


Figure 3. Schematic diagram of charge trapping process for cells based on (a) bare TiO<sub>2</sub> film (b) Ni doped TiO<sub>2</sub> film and energy states changing of the semiconductors (c) and (d) shows, after the  $r=r_n$ ,  $J_{sc}$  decrease exponentially with the Ni concentration. The maximum position of the efficiency also correspond to the position of maximum  $J_{sc}$ .

### CONCLUSIONS/RECOMMENDATIONS

The reproducible results presented in this work clearly demonstrate that the performance of DSPECS based on TiO<sub>2</sub> thin film could be enhanced by doping Ni with TiO<sub>2</sub>. There were enough evidences to explain the interaction of Ni with the TiO<sub>2</sub> surface and enhancement of the efficiency and photo voltage of the Ni doped cells. In the low level doping of Ni, the recombination is better suppressed by decreasing the carrier trapping rate, which is one of the main causes of recombination. The variation of the energy states and band gaps are done by Ni doping, directly affected to the photo voltage enhancement. There is no evidence that Ni leaches into the electrolyte. Since the prescription adopted to prepare TiO<sub>2</sub> films in this investigation is not optimized as in the procedures published (Gratzel 2001), we believe that the performances of the Ni doped cells can be further improved by optimizing the TiO<sub>2</sub> film casting procedure.

### REFERENCES

- Gratzel, M. (2001) Photoelectrochemical cells, *Nature* 414, 338-344.
- Mora-Sero, I., and Bisquert, J., (2003), Fermi Level of Surface States in TiO<sub>2</sub> Nanoparticles, *Nano Lett.* 3(7) 945-949.
- Murphy, A.B. (2007) Band-gap determination from diffuse reflectance measurements of semiconductor films, and application to photoelectrochemical water-splitting, *Solar Energy Materials & Solar Cells* 91, 1326-1337.
- Simmons, J.G., Taylor, G.W., (1971) Nonequilibrium steady-state statistics and associated effects for insulators and semiconductors containing an Arbitrary distribution of traps, *Physical Review B* 4(2) 502-511.
- Wijayarathna, T.R.C.K., Aponsu, G.M.L.P. Ariyasinghe, Y.P.Y.P, Premalal, E.V.A Kumara, G.R.R. and Tennakone, K. (2008) A high efficiency indoline-sensitized solar cell based on a nanocrystalline TiO<sub>2</sub> surface doped with copper, *Nanotechnology* 19 (48) 485703.
- Wu, S.J., Chen, C.Y., Li, J.Y., Chen, J.G., Lee, K.M., Ho, K.C., Wu, C.G., (2010) Carbazole Containing Ru-based Photo-sensitizer for Dye-sensitized Solar Cell, *J. Chin. Chem. Soc.* 57(5A) 1-4.