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Journal of Photochemistry and Photobiology A: Chemistry 170 (2005) 273–278

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

The role of n–p junction electrodes in minimizing the charge recombination and enhancement of photocurrent and photovoltage in dye sensitized solar cells

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Received 19 April 2004; received in revised form 9 July 2004; accepted 31 August 2004

Abstract

The composite electrode comprising n-type TiO_2 and p-type NiO oxides when sensitized with Ru-dye showed short-circuit photocurrent (I_{sc}) of 17 mA/cm^2 and open-circuit photovoltage (V_{oc}) of 730 mV compared to I_{sc} of 12 mA/cm^2 and 700 mV for TiO_2 electrodes. Formation of a n–p junction between TiO_2 and NiO oxide layers contributes to the enhanced photocurrent, photovoltage, fill factor and efficiency. In addition to the junction effect, NiO acts as a barrier for charge recombination leading to higher cell performance. The efficiency of the NiO coated TiO_2 solar cell is 30% more than that of bare TiO_2. The negative shift of the flat-band potential of the NiO coated TiO_2 electrode compared to TiO_2 also could be one of the reasons for higher photovoltage observed for TiO_2/NiO electrode. The highest cell efficiencies were obtained immersing TiO_2 thin films in Ni^{2+} solution and converting them to NiO by firing and the optimum NiO coating thickness was found to be only a few angstroms. The energy levels of the excited dye and the band positions of TiO_2 and NiO suggest that the electron transfer from the excited dye to the underlying n-type oxide layer occurs by tunneling through the p-type NiO layer.

Keywords: n–p Junction; TiO_2; NiO; Dye sensitization; Charge transfer

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1. Introduction

Dye sensitized photoelectrochemical cells (PEC) constructed using nano-porous films are gaining recognition as promising photovoltaic devices for conversion of solar energy [1–5]. The efficient sensitization of semiconductor nanocrystallites with inorganic and organic dyes have been demonstrated [6–8]. PECs with Ru-bipyridyl dye coated TiO_2 films in I^-/I_3^- redox electrolyte generate short-circuit photocurrents (I_{sc}) at near unity incident photons to photocurrent conversion efficiencies (IPCE) and 10% energy conversion efficiency (η) has been achieved [3]. The large electron effective mass in TiO_2 found to be one of the major reasons for its higher energy conversion efficiency as high electron mass prevents the leakage of trapped electrons into the electrolyte interface [9]. In spite of better cell performance of dye sensitized TiO_2, during the past few years, reports have been appeared in literature that describe the construction of DS PECs from modified TiO_2 electrodes [10–13]. The attempts have been made to increase the solar power efficiency minimizing the charge recombination processes. In order to minimize the charge recombination, it is imperative control of electron transfer from nanocrystalline films and conducting ITO to redox medium. The back electron transfer from TiO_2 and other oxides has been minimized using a thin insulating layer on the semiconducting nanocrystalline films [9–11].

The electrode material, film morphology, photophysical and structural properties of the sensitizer and the redox couple used are found to be the major factors, which control the overall cell performance. In semiconductor suspension, the presence of Schottky barrier helps charge separation, however in nanocrystalline semiconductor films, an ideal Schottky barrier is absent and hence the driving force for charge

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1010-6030/$ – see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.jphotochem.2004.08.023

separation is absent [14–16]. However, a potential gradient arising from varying degree of electron accumulation within the semiconductor particles acts as a driving force for transport of injected electrons across the films [17–20]. Hence, better charge separation could achieve if a potential gradient could be introduced across the film and the presence of a n–p junction would be one of the methods to introduce such a potential gradient. In such a way, the introduction of a n–p junction in DSC would suppress the dark current arising from the reduction of the redox electrolyte at the semiconductor surface, improving the photovoltage. In an earlier publication, we constructed a n–p junction using n-type SnO_2 and p-type NiO and explained how the NiO layer on SnO_2 could improve the cell efficiency by suppressing the leakage of trapped electrons to the electrolyte interface [21]. The aim of the present study is to construct a different n–p junction for dye sensitized solar cells with n-type TiO_2 and p-type NiO and compare the results with SnO_2/NiO solar cell.

2. Experimental

Thin films of nanocrystalline TiO_2 were prepared mixing p-25 Degussa (1.0 g), HNO_3 (5.0 ml) and H_2O (1.0 ml) in an agate motor and added few drops of carbowax and polyethylene glycol. The final TiO_2 slurry was applied on cleaned conducting glass by doctor blade method and sintered in air at 550 °C for 30 min. For NiO coating, TiO_2 coated plates were then immersed in an aqueous solution of nickel sulphate ($\sim 0.2 \times 10^{-2}$ mol l^{-1}) for 60 min and washed with distilled water to remove any nickel sulphate remaining in the film and sintered at 550 °C for 30 min (method 1). The white TiO_2 films turned slightly yellowish colour after coating a thin layer of NiO. Also thin films of NiO coated TiO_2 were prepared mixing TiO_2 and Ni^{2+} in an agate motor and thin films were fabricated by doctor blade method (method 2). The NiO films on conducting glass were prepared using NiO powder and doctor blade method. Films deposited on CTO glass plates were coated with the dye *cis*-dithiocyanato [*N*-bis(2-2′-bipyridyl-4,4′-dicarboxylic acid)] Ru(II) by immersing the plates in a warm (~80 °C) alcoholic solution (3.0×10^{-3} mol l^{-1}) of this dye for 4 h. After rinsing the plate with acetonitrile and drying, the solar cell was formed by clamping the dyed film surface to the counter-electrode (lightly platinized CTO glass plate) and filling the capillary space with the electrolyte (0.6 M dimethylpropyl imidazolium iodide + 0.1 M LiI + 0.05 M I_2 + 0.5 M *t*-butyl pyridine in methoxyacetonitrile).

The *I*–*V* characteristics of the cells and the incident photon to photocurrent conversion efficiencies were recorded using a solar cell evaluation system (JASCO, CEP-25BX). Nickel content in the film was estimated by atomic absorption spectroscopy (AAS) after extracting Ni with concentrated HNO_3 (film is scraped off and digested with concentrated HNO_3 for several hours). The flat-band potential of the oxides were determined from Mott–Schottky plots (i.e. a plot of C^{-2} versus *V*, where *C* was the capacitance and *V* was the potential across the space charge layer). To measure the capacitance, oxide coated plates were immersed in Na_2SO_4 solution and the capacitances were measured as a function of the potential across the space charge layer at frequencies of 500 Hz and 1 kHz. Electron micrographs are taken with a LEO-1400 model scanning electron microscope (SEM). X-ray diffraction (XRD) measurements were done using Shimadzu-XD-7A.

3. Results and discussion

The photovoltaic performance of the NiO coated TiO_2 nanocrystalline films were done by the following methods. *I*–*V* characteristics of the solar cells constructed with TiO_2 and NiO coated TiO_2 (TiO_2/NiO) under 1,5 AM illumination are shown in Fig. 1. The solar cell fabricated entirely with NiO electrode (not shown in Fig. 1) sensitized with Ru-dye shows a cathodic photocurrent of 25 μA/cm^2 and a cathodic photovoltage of 50 mV at the illumination intensity of 1000 Wm^{-2} while the solar cells fabricated with TiO_2 and TiO_2/NiO show photoanodic behaviour. According to the device performance shown in Fig. 1, increase in both I_{sc} and V_{oc} was clearly noticed for the DS cells made from nanocrystalline films of TiO_2/NiO compared to uncoated TiO_2 with Ru-dye. i.e. DS cells made from nanocrystalline films of TiO_2 with Ru-dye give V_{oc} of the order ~675 mV, I_{sc} of ~12.0 mA/cm^2 and efficiency (η) of the order 6.1% with a fill factor of 64%. For the DS cells made of NiO coated TiO_2, V_{oc} (~730 mV) and I_{sc} (~16.7 mA/cm^2) were noticed at the same illumination intensity and the calculated fill factor and efficiency are 66.5% and ~7.8%, respectively. From the results presented above, it is clearly seen that the addition of NiO to TiO_2 films enhances the I_{sc}, V_{oc} and η by about 16%, 4% and 30%, respectively compared with uncoated TiO_2 electrode. For dye coated TiO_2 electrode, 27.2% IPCE value was observed at

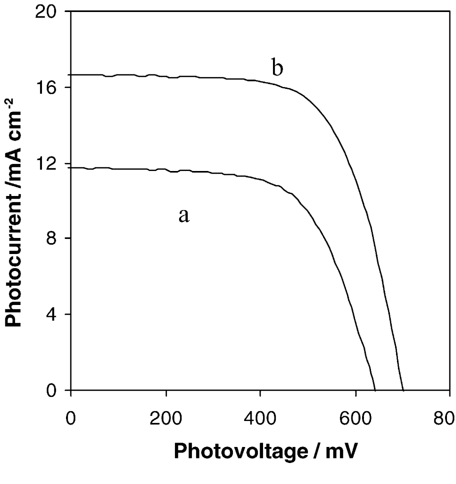

Fig. 1. *I*–*V* characteristics of the DS made from: (a) TiO_2 and (b) TiO_2/NiO at an illumination intensity of 1000 Wm^{-2} 1.5 AM.

590 nm while for TiO_2/NiO electrode, 36.4% IPCE was noticed at the same wavelength. For the results presented in Fig. 1, electrodes were prepared by method 1 because both preparation methods gave the comparable results.

Device performances of the NiO coated TiO_2 electrodes were found to be highly dependent on the NiO amount and the variation of I_{sc} and V_{oc} with the variation of NiO percentage are shown in Table 1. As shown in Table 1, with the increase of NiO content, I_{sc} increases and the maximum I_{sc} was noticed when the NiO amount was ~4% (w/w). Increase in NiO amount further, decreases the I_{sc} gradually. However, V_{oc} was found to increase as the amount of NiO increases and at the maximum I_{sc} the corresponding V_{oc} was ~730 mV. The maximum value of I_{sc} also corresponds to the position of maximum efficiency and contains 1.0 g of TiO_2 and ~0.03–0.04 g of NiO. The SEM images of TiO_2 and NiO coated TiO_2 are shown in Fig. 2. Interconnected aggregates of TiO_2 crystallites appeared clearly in both SEM images but did not reveal any distinguished difference between TiO_2/NiO (4.0%) and TiO_2 films. This could be due to fact that a very thin NiO layer is formed on TiO_2 that could not be seen by SEM analysis. Therefore, the thickness of the NiO layer at the maximum solar cell efficiency was estimated from the amount of Ni^{2+} added which is equal to 13.3 μmol of NiO/m^2 of TiO_2 taking the surface area of TiO_2 as 40 m^2/g. The calculated thickness of the NiO layer on TiO_2 was 0.15 nm (or 1.0 mg of NiO/m^2 of TiO_2) considering the bulk density of NiO as 6.57 g/cm^3. From the above results, it can be concluded that a very thin NiO layer is formed around TiO_2 nanocrystallites. The XRD pattern shown in Fig. 3 did not resolve NiO peaks for the TiO_2/NiO electrode when the NiO contenet = 4% or the NiO layer thickness is 0.15 nm. Since no diffraction peaks were observed for the NiO of the composite film of TiO_2/NiO (4%), the XRD results justify the formation of a thin NiO layer on TiO_2 particles. However, on increasing the NiO%, only NiO and TiO_2 peaks appeared indicating the absence of mixed oxide.

The dark *I*–*V* characteristics of the cells made of NiO, TiO_2 and TiO_2/NiO in the forward and reverse bias are shown in Fig. 4. As shown in Fig. 4, NiO, TiO_2 and TiO_2/NiO (4%) electrodes show good rectification behaviour, which is needed for functioning as a photovoltaic device. The NiO electrode show rectification behaviour even though the solar cells made of NiO electrodes shows poor efficiencies. Thus, the dark current does not necessarily indicative of the photocurrent and the lower efficiency of NiO electrode could be due to inappropriate redox potentials of the redox couple and the unsuitable valence band (VB) potentials as described in [21,22]. The TiO_2 electrode shows slightly a better rectification than that of NiO coated TiO_2 films under dark conditions. The anodic onset voltage of TiO_2/NiO is less than that of bare TiO_2, which could be due to slight increase of series resistance as a result of introduction of NiO layer. However, under illumination, a better diode behaviour was noticed for NiO coated TiO_2 than TiO_2 alone and hence under illumination, the TiO_2/NiO electrode behaves differently. Fig. 5 shows the Mott–Schottky plots of NiO, TiO_2 and TiO_2/NiO and the negative shift of flat-band of TiO_2/NiO (4%) is clearly noticed. It is clearly seen the p-type behaviour for NiO electrodes while for TiO_2 electrodes n-type behaviour was noticed. TiO_2/NiO (4%) electrode also behaves similar to n-type but the flat-band position of TiO_2 has been shifted from −0.18 to −0.32 eV at pH 5.5. Hence, the negative shift of flat-band potential of TiO_2/NiO (4%) results in increase in V_{oc}. The calculated conduction band (CB) and valence band potentials of NiO,

Table 1
Solar cell performance of TiO_2 and NiO coated TiO_2 with the variation of NiO percentage

	V_{oc} (mV)	I_{sc} (mA/cm^2)	FF (%)	Efficiency (%)
TiO_2	675	12.0	63.9	6.09
TiO_2/NiO (2%)	703	16.0	67.3	6.61
TiO_2/NiO (4%)	730	16.7	66.4	7.74
TiO_2/NiO (6%)	756	15.9	61.2	6.00
TiO_2/NiO (10%)	761	7.8	55.9	3.36
TiO_2/NiO (15%)	788	5.5	52.5	2.29
TiO_2/NiO (25%)	800	4.1	49.5	1.6

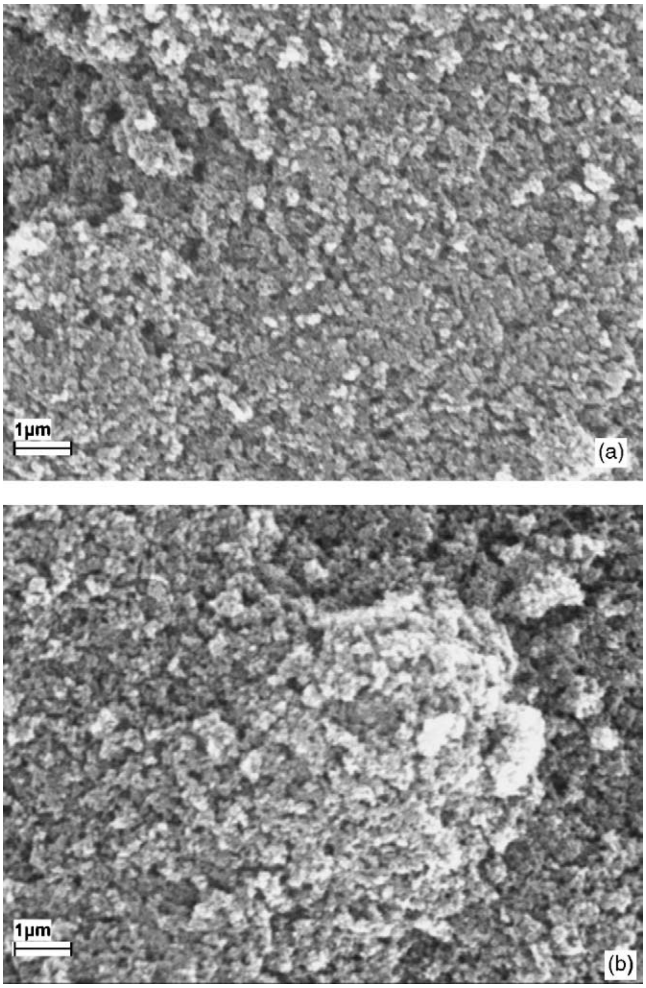

Fig. 2. SEM images of (a) TiO_2 and (b) TiO_2/NiO (4%).

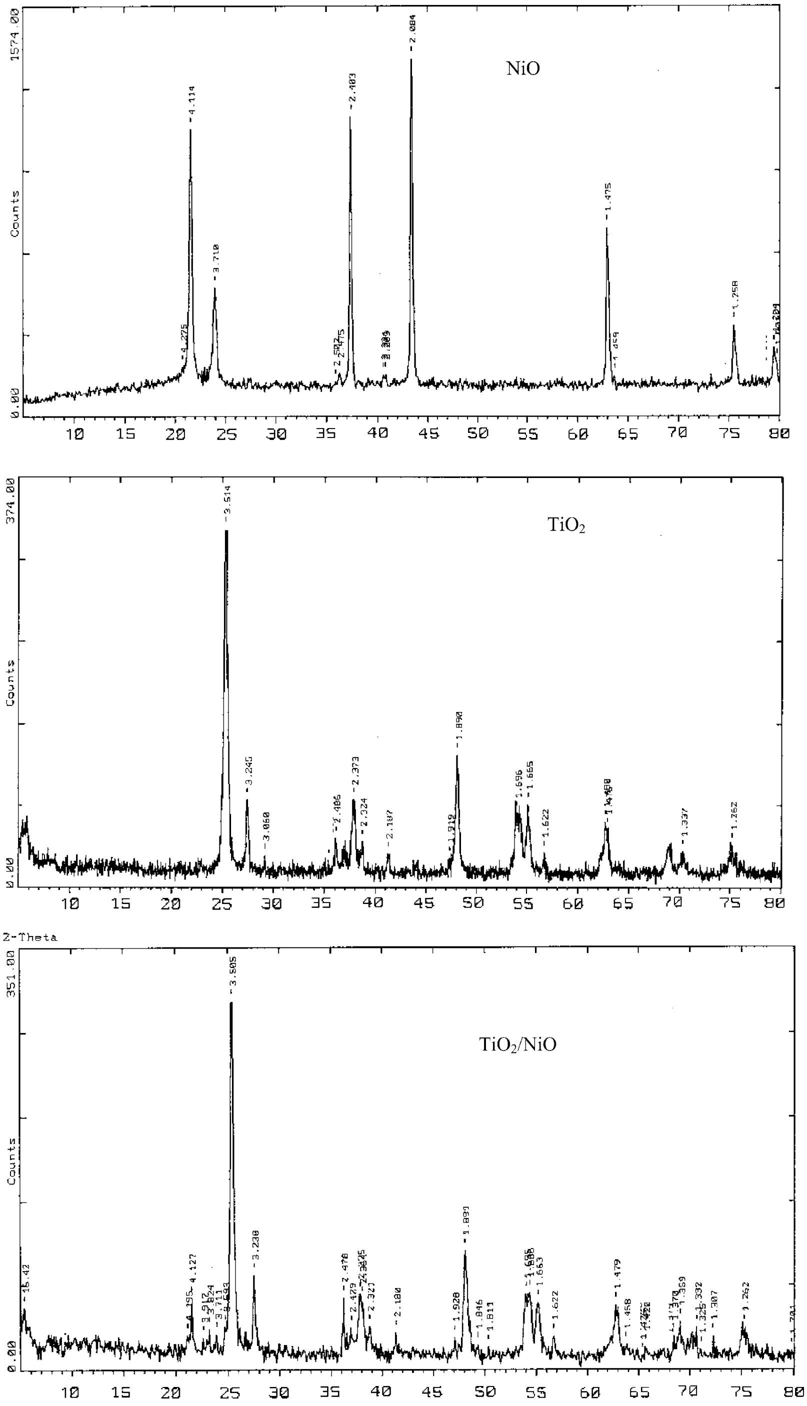

Fig. 3. XRD patterns of NiO, TiO_2 and TiO_2/NiO (4%).

TiO_2, and TiO_2/NiO (4%) from Mott–Schottky are given in Table 2.

In an earlier publication, we reported that the n–p junction formed between n-type SnO_2 and p-type NiO leads to enhance solar cell performance when sensitized with Ru-dye [21]. The solar cells made from nanocrystalline films of SnO_2 with Ru-dye give V_{oc} of the order ~330 mV, I_{sc} of ~2.8 mA/cm^2 and very low efficiencies i.e. of the order 0.5% with a fill factor of 45%. For the DS cells made of SnO_2 and NiO composite, a dramatic increase in V_{oc} (~510 mV) and I_{sc} (~8.6 mA/cm^2) was noticed at the same illumination intensity and the calculated fill factor and efficiency are 60% and ~2.7%, respectively. Similarly, the results presented above for TiO_2/NiO electrode shows the enhancement of I_{sc}, V_{oc} by 16% and 4%, respectively for the dye sensitized solar cells when they were fabricated coating of a NiO layer on TiO_2. Therefore, one can conclude that the reason for enhanced solar cell performance of TiO_2/NiO could be the same as

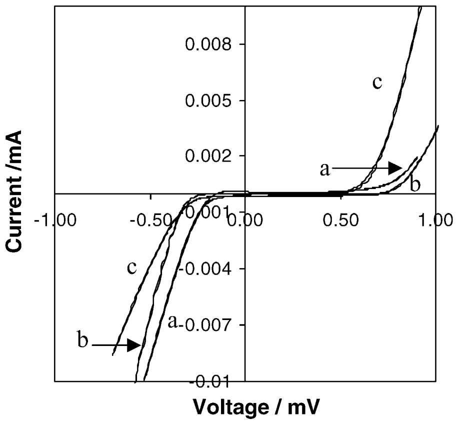

Fig. 4. Dark *I*–*V* characteristics of the DS made from: (a) NiO, (b) TiO_2 and (c) TiO_2/NiO.

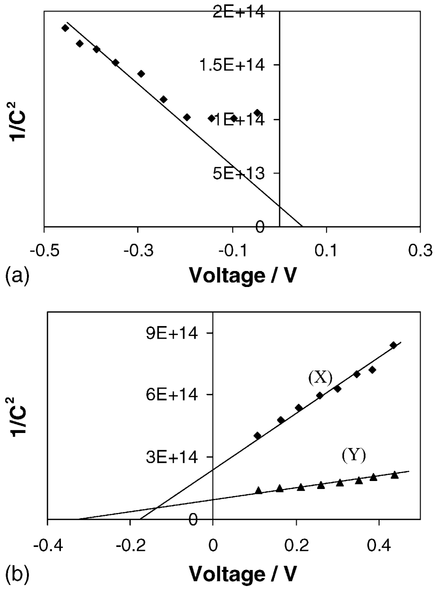

Fig. 5. (a) Mott–Schottky plot of NiO, (b) Mott–Schottky plots of TiO_2 (*X*) and TiO_2/NiO (*Y*). Capacitances were displayed only for frequency of 1.0 kHz and the pH of the solution was at 5.5.

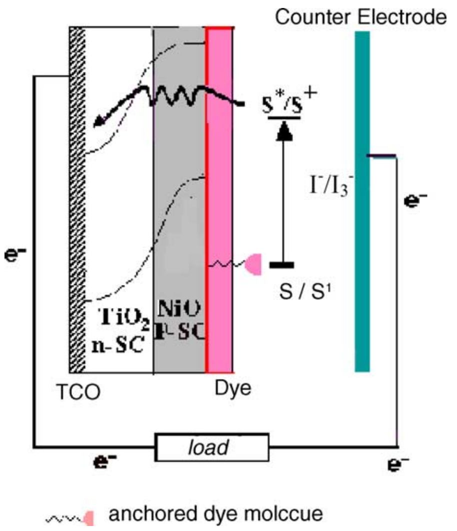

Fig. 6. Schematic diagram illustrating the energy levels of TiO_2, NiO and the ground and excited energy levels of the Ru-dye.

for SnO_2/NiO and the possible charge transfer mechanism and the function of the n–p junction electrodes are described below.

It has been reported, that the coating of an insulating oxide layer on nanocrystalline thin films results in increase in I_{sc} and V_{oc} in which an insulating layer acts as a barrier for charge recombination of the transferred electrons [9,13]. Similarly, the function of NiO could be explained using the same arguments. Coating of a thin NiO layer on TiO_2 nanocrystalline thin films leads to the formation of n–p junction and the electrodes were fabricated in such a way, that the inner TiO_2 particles were surrounded by an outer NiO shell which cause dye adsorption on NiO layer than TiO_2 particles. According to the CB and VB potentials of TiO_2, NiO and the ground and excited levels of the Ru-dye shown in Fig. 6, photogenerated electrons of the dye adsorbed on NiO layer cannot be transferred to the CB of NiO as the CB potential level is higher than the dye excited level. The other possibility is that the energized electrons transfer to the CB of TiO_2 via tunneling through the thin NiO layer. Once the electrons were transferred to the CB of TiO_2 from the excited dye, the NiO layer could act as a barrier layer for electron recombination leading to higher IPCE. Tunneling of electrons through a thin NiO would be facilitated being NiO a p-type oxide. i.e. less scattering of electrons is expected via tunneling through NiO because the electrons are the minor carriers in such p-type oxide.

Table 2
Calculated VB and CB positions of NiO, TiO_2 and TiO_2/NiO (4%) by Mott–Schottky plot

	VB (eV) (NHE)	CB (eV) (NHE)
TiO_2	3.02	−0.18
NiO	−3.00	0.50
TiO_2/NiO	2.88	−0.32

The pH of the solution was 5.5.

Additionally, in nanocrystalline semiconductor films an ideal Schottky barrier, which helps charge separation, is absent resulting in less efficient charge separation [14–16]. However, a potential gradient arising from varying degree of electron accumulation within the semiconductor particles acts as a driving force for the transport of injected electrons across the films. The inclusion of a potential gradient by a n–p junction of TiO_2–NiO would have directed the electron traverse from NiO particles to TiO_2 particles effectively. Therefore, the function of a thin NiO layer on TiO_2 particles are: (a) it acts as a barrier for the recombination of electrons in CB of TiO_2 and the oxidized dye/electrolyte interface; (b) the n–p junction that formed between TiO_2 and NiO would have facilitated the electron transfer from NiO to TiO_2.

According to the charge transfer mechanism described above, n–p junction would have facilitated the charge transfer from p-type NiO to n-type TiO_2 and the band positions of NiO and TiO_2 allows charge transfer from NiO to TiO_2 as shown in Fig. 6. In order to confirm that the electrons transfer occurs from NiO to TiO_2, a solar cell was fabricated coating a thin TiO_2 layer on NiO films. The NiO films were fabricated on conducting glass by doctor blade method followed by coating of a TiO_2 layer by immersing in TiO_2 colloid suspension. The DS solar cell of NiO/TiO_2 (NiO/TiO_2 denotes that the DS cells made coating of TiO_2 on NiO particles) sensitized with Ru-dye gives V_{oc} of the order 150 mV, I_{sc} of 0.1 mA/cm^2 and very low efficiencies. The V_{oc}, I_{sc} and efficiency values for NiO/TiO_2 are negligible to the corresponding values of TiO_2/NiO electrodes. The reason for the low efficiency could be due to fact that the NiO/TiO_2 electrode is fabricated in such a way, that NiO is contacting the ITO glass and in the NiO–TiO_2 p–n junction, dye molecules are mainly adsorbed on outer TiO_2 layer. As the CB of NiO position is higher than that of TiO_2, the electrons injected from the excited dye molecules to the CB of TiO_2 should surmount the NiO energy barrier and compete with the recombination at the interface. Therefore, the relaxed electrons in the CB of TiO_2 could not tunnel to the NiO layer efficiently and reach the conducting glass. Considering all these factors, it can be concluded that the charge transfer occurs from NiO to TiO_2 traversing electrons through NiO layer.

The enhancement of solar cell performance presents here for the TiO_2/NiO n–p junction electrode is comparable to that of using an insulating oxide layer on semiconducting oxide crystallites films. The advantage of using p-type oxide layer is that it introduces a potential gradient across the film despite it acts as a charge recombination barrier. However, such a potential gradient is not generated by the introduction of an insulating layer and therefore the use of n–p junction electrode for dye sensitized solar cells would be preferred over the use of an insulating oxide layer.

4. Conclusion

The effects of n–p junction formed between TiO_2 and NiO layer for minimizing charge recombination were studied. The n–p junction formed between TiO_2 and NiO facilitate the efficient electron transfer and hence increase in both I_{sc} and V_{oc} are noticed. The n–p junctions of TiO_2/NiO and SnO_2/NiO behave similarly and such n–p junction solar cells work better if the dye adsorption occurs on the p-type oxide and the possible charge transfer mechanism is discussed. In addition to the junction effect, the NiO layer acts as a barrier for charge recombination leading to higher IPCE.

Acknowledgement

We thank Dr. C.P.K. Udawatta for XRD analysis.

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