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Employing NiO as a hole collector in solid-state dye-sensitized solar cell

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Abstract

A solid-state dye sensitized solar cells (DSSC) comprising of p-type NiO thin layer on TiO2 was fabricated in which the dye is adsorbed on the p-type oxide and the thin NiO layer acts as a hole collector as well as a barrier for charge recombination. DSSC with NiO coated TiO2 electrode with Ru-dye delivers Isc = 0.15 mA and Voc = 480 mV. It was shown that the p-type oxide materials could be successfully used to construct DSSC and the plausible charge transfer mechanism is discussed.

1. INTRODUCTION

In dye-sensitized solar cells, dye is regenerated using a suitable liquid redox couple. i.e I^-/ I_3^- [1-3]. In such solar cells, the liquid electrolyte tends to evaporate since perfect sealing of solar cells is not possible. The disadvantages of using liquid electrolyte have been overcome by replacing the liquid electrolyte with room temperature molten salts, inorganic p-type semiconductors, ionic conducting polymers and organic hole transport materials [4-7]. However, the dye-sensitized solid-state solar cells (DSSC) using p-type semiconductors often met problems of short-circuit and mass transport limitations of the ions resulting in low conversion efficiencies compared with the liquid version. In DSSC where p-type semiconductors used as hole collectors, the hole collector is deposited on the dyed dense TiO_2 layer [5]. Only a few types of p-type semiconductors have been tested as solid hole collectors i.e. CuSCN [4], CuI [8], because of the difficulty of identification of a suitable hole collector and its deposition. Although CuSCN and CuI possess appropriate band gap and band positions, both lack stability and tend to degrade in short times. In a conventional DSSC, the device is fabricated in such a manner that the dye is adsorbed on n-type oxide layer and the hole collector is deposited on the dyed oxide layer. Hence, finding a suitable hole collector with required properties is a great challenge, i.e. appropriate band gap, band positions and method for its deposition preserving the properties of the adsorbed dye layer. It is also needed to have proper contacts between dye and the p-type materials.

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The disadvantage of such solar cells is that it limits the choice of a suitable hole collector. In this respect, p-type oxide semiconductors have never been tested as solid hole collectors because of the lack of suitable p-type oxide semiconductors with appropriate properties to be used as hole collectors and also difficulties of fabrication of oxide semiconductor on dyed TiO2. In this communication, we report the fabrication of DSSC using p-type NiO as a solid hole collector. In the case where p-type oxide materials are used to fabricate DSSCs, dye is adsorbed on the p-type materials itself leading to better contact between dye and the p-type material and hence better charge separation. In addition, availability of different p-type oxide materials provides opportunity of optimizing the electrode properties of n-p junction. Therefore, using the p-type oxide semiconductors described in this communication could solve some of the problems encountered in fabrication of DSSCs.

2. EXPERIMANTAL

Nanocrystalline dense films of TiO_2 were prepared by the procedure described below. Titanium tetra-isopropoxide (5ml, Aldrich) mixed with acetic acid (5.5 ml) and propan-2-ol (20 ml) followed by addition of water dropwisly (5 ml). Few drops of the suspension were spread on a 150°C heated conducting tin oxide glass plate. After puffing off the loosely bound crust, the suspension was again spread. After three such cycles, the film was sintered at 550°C for 15 minutes and the loose crust on the surface was wiped off. The entire process was repeated until a film ~ 10 μm is formed. For NiO coating, the TiO_2 electrodes were first dipped in 1×10^{-2} M $NiSO_4$ solution for 3 hours, washed with distilled H_2O to remove excess Ni^{2+} and finally sintered at 400°C for 30 minutes. Once a thin uniform layer of NiO was coated on TiO_2 particles, another thin NiO layer was applied by doctor blade method to confirm the full coverage of TiO_2 crystallites [9]. The films were dyed keeping them immersed in a 5.0×10^{-4} M solution of cis-bis(thiocyanate)bis(2,2'-bipyridyl 4,4'-dicarboxylate) ruthenium(II) in ethanol for 6 hours. On the dyed TiO_2/NiO layer, a thin layer of graphite was applied for better contact between the electrode and the back contact. Pt sputtered conducting tin oxide glass plate was used as the back contact. The energy conversion efficiency was measured under simulated sunlight (AM 1.5, 100 $mWcm^{-2}$ illumination) and the incident photons to photocurrent conversion efficiency (IPCE) was measured using a solar cell evaluation system. Rectification curves in the dark were recorded using dyed TiO_2/NiO electrodes. The energy conversion efficiency was measured under simulated sunlight (AM 1.5, 1000 Wm^{-2} illumination).

3. RESULTS AND DISCUSSION

NiO is a p-type semiconducting oxide, which has been used for dye-sensitized solar cells [10-12]. A solar cell constructed with a NiO thin film and Ru dye, in the presence of an electrolyte shows very poor cathodic photocurrent of ~ 25-30 μA and photovoltage of 50 mV. The p-type nature of the NiO is evidenced by the generation of a cathodic photocurrent and Mott-Schottky analysis as explained in reference [13]. Since NiO acts as a p-type oxide, it can be used as a hole collector in construction of DSSCs. Figure 1 shows the I-V characteristic under 100 mW cm^{-2} visible band illuminations of the DSSC constructed coating of a thin NiO layer on the dense TiO_2 film and the dye which is adsorbed on NiO layer. The devise had an open-circuit voltage (Voc) of 480 mV and a short-circuit photocurrent (Isc) of 0.15 mA cm^{-2}. The maximum energy conversion efficiency and the fill factor derived from the Figure1 are 0.032% and 47.6% respectively. The solar cells made without NiO on the TiO_2 crystallites did not give measurable Isc and Voc at the same illumination intensity confirms that the NiO function as a hole collector The electrode described above consists of both thin NiO layer on TiO_2 particles formed by dip coating method and the second NiO layer formed by doctor blade method. The electrode, where the NiO coating was done using doctor blade method only showed better Isc values but poor fill factor which could be due to improper or week contact between TiO_2 and NiO particles. It was noticed that for the electrodes containing only a thin NiO layer formed on TiO_2 particles by dip coating in Ni^{2+} solution increases the fill factor, but lower photocurrent due to poor dye loading. Therefore, it is imperative to have both a thin NiO layer formed by dip coating method and the second NiO layer formed by doctor blade method for better Isc and fill factor.

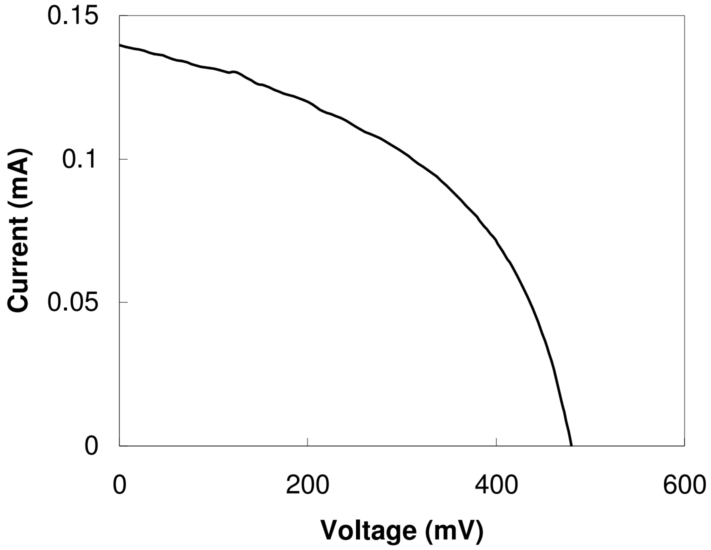


Figure 1. I-V characteristics of the cell TiO_2/NiO/dye at illumination intensity of 100 mWcm^{-2} 1.5AM

The dark I-V curve in the forward and reverse bias for the cell constructed with TiO_2/dye and TiO_2/NiO/dye are shown in Figure 2. The diode characteristic, which is needed for functioning as a photovoltaic device, is absent for the TiO_2/dye while for TiO_2/NiO/dye electrode enhanced diode behaviour was clearly noticed. Enhanced rectification of the TiO_2/NiO/dye junction is observed when the cell is constructed with the dye than when the cell is constructed with no dyes. The photocurrent action spectra of the TiO_2/NiO/dye cell gives a peak at ~550 nm with the maximum IPCE 6% (corrections were not made for losses) and matches the absorption spectra of Ru-dye.

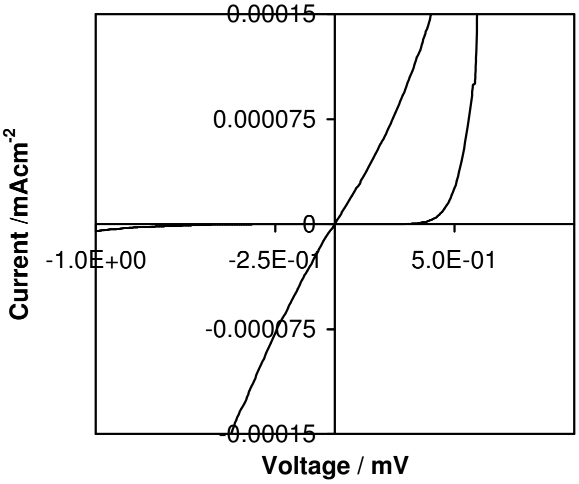
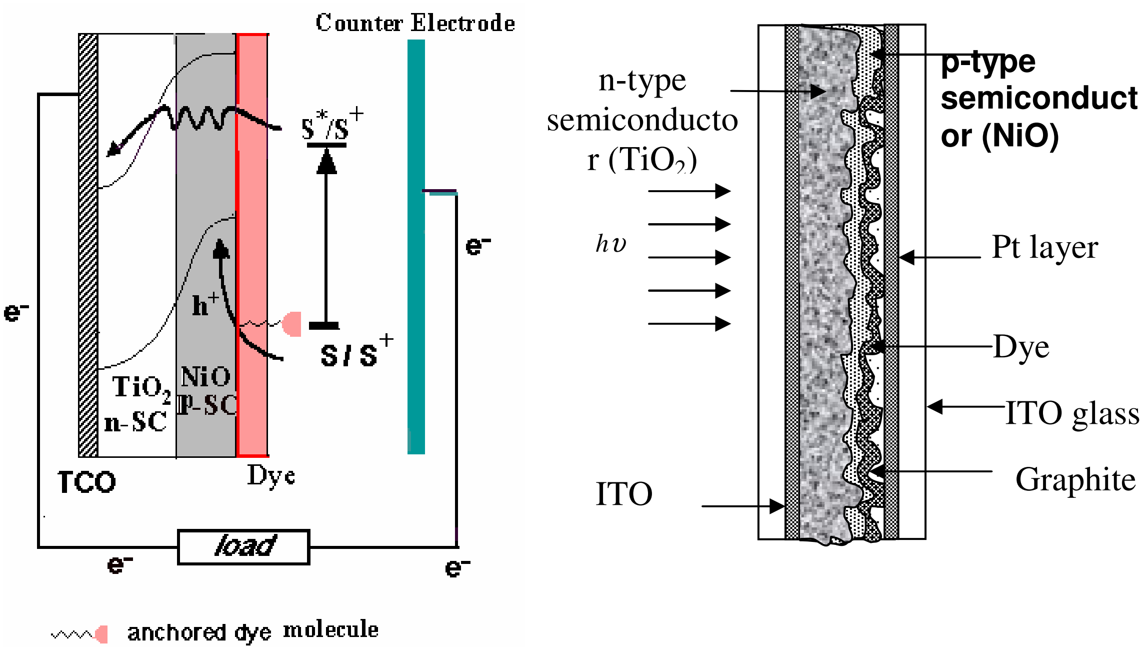


Figure 2. The rectification curves for (a) TiO_2/dye and (b) TiO_2/NiO/dye

From the results presented above, it is clearly seen that the NiO layer on TiO_2 nanocrystallites acts as a hole collector. The mechanism of photocurrent generation and the device function can be explained as follows; Figure 3a shows the band positions of TiO_2 and NiO alone with the ground and excited states of the dye and the direction of charge flow. The schematic diagram of the device is shown in Figure 3b. The device structure consists of a dense TiO_2 layer, which is covered by a thin NiO layer and the dye is adsorbed on NiO layer. NiO is a p-type semiconductor having band gap of 3.55 eV with conduction band (CB) position at –3.0 eV and valence band (VB) at 0.1 eV [10-13]. The cell constructed with TiO_2/dye/graphite did not show any photocurrent confirms that the electrode without NiO does not perform solar cell characteristics. The amounts of dye adsorbed were found to be 5.125 X 10^{15} and 4.885 X 10^{16} molecules cm^{-2} on TiO_2 and TiO_2/NiO respectively. From the dye adsorption amount and the way the solar cell is constructed, it can be assumed that most of the dye is adsorbed on the NiO layer. For photocurrent generation, first, the light is absorbed by the adsorbed dye on NiO layer generating excited states of dye. The electron in the excited state of the dye is not energetic enough to transfer electrons to the CB of NiO as the CB position of NiO is well above the excited state potential of the dye.



(a)

(b)

Figure 3(a) Energy level diagram showing the band positions of TiO_2, NiO, ground and excited state energy levels of the dye. **(b)** Schematic diagram of the TiO_2/NiO/dye solar cell.

However, it has been reported tunneling of energetic electrons through an insulating MgO layer in dye sensitized solar cells of SnO_2/MgO/Dye [14] and TiO_2/MgO/Dye [15-16]. It has been shown that the thin insulating layer on SnO_2 and TiO_2 acts as a barrier for charge recombination as well as electron tunneling media. In a recent issue, we reported enhanced solar cell performance using n-p junction electrode made of SnO_2 and NiO in dye sensitized solar cells with liquid electrolyte [13]. Similarly, the energetic electrons generated in dye on NiO layer are injected to the CB of TiO_2 traversing through the NiO layer while the photooxidised dye is reduced by transfer of electrons from the VB of NiO thus producing a photocurrent through an external circuit. The graphite layer completes the circuit, connecting the counter electrode and the NiO layer. The thickness of the NiO layer was calculated from the NiO present and found to be roughly 1.2 nm, thus tunneling of electrons across such a thin layer is probable. This is the first report on fabrication of dye sensitized solid-state solar cell, using p-type semiconduting oxide as a hole collector. Apart from it's hole collector behaviour, n-p junction formed between TiO_2 and NiO would facilitate the charge separation and the thin NiO layer could act as a barrier layer for charge recombination between the reduced dye and the electrons in the CB of TiO_2 as shown in Figure 3a.

The Isc and efficiency values of the DSSC constructed with NiO layer as a hole collector are inferior to the Isc and efficiency values of the cell constructed with CuI as hole collectors. The lower efficiency could be due to the fact that an efficient injection of electron may not possible with NiO, but with a suitable oxide, an efficient electron injection may achieve and hence higher Isc could be expected. The advantage of using p-type oxide material as a hole collector is that better contact between the dye and the p-type material could achieve where as in the case of CuI, better contact between dye and the hole collector is not possible. In addition, availability of different p-type oxide materials provides opportunity of optimizing the electrode properties of n-p junction. Therefore, using the p-type oxide semiconductors described in this communication could solve some of the problems encountered in fabrication of DSSCs.

4. CONCLUSIONS

In conclusion, for the first time, we described fabrication of a DSSC using p-type oxide material. The Isc and the cell efficiency of the solar cell constructed using NiO are lower than that of the best cell performance obtained for the DSSC reported to date. However, by the method described in this communication and with a suitable p-type oxide semiconductor, one could fabricate a much stable dye sensitized solid-state solar cell with an enhanced efficiency.

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