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Solid-state dye-sensitized solar cell with p-type NiO as a hole collector

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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 electrodes with Ru-dye delivers $I_{sc} = 0.15$ mA and $V_{oc} = 480$ 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.

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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

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used as hole collectors, the hole collector is deposited on the dyed dense TiO₂ 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 time. 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. 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. Experimental

Nanocrystalline dense films of TiO₂ were prepared by the procedure described below. Titanium tetra-isopropoxide (5 ml, 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 puffed off the loosely bound crust, the suspension was again spread. After three cycles, the film was sintered at 550°C for 15 min and loose crust on the surface was wiped off. The entire process was repeated until a film ~10 μm is formed. For NiO coating, the TiO₂ electrodes were first dipped in 1.0×10^{-2} M NiSO₄ solution for 3 h, washed with distilled H₂O to remove excess Ni²⁺ and finally sintered at 400°C for 30 min. Once a thin uniform layer of NiO was coated on TiO₂ particles, another thin NiO layer was applied by doctor blade method to confirm the full coverage of TiO₂ 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 h. On the dyed TiO₂/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 mW cm⁻² illumination) and

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