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Fabrication and characterization of thin Nb_2O_5 blocking layers for ionic liquid-based dye-sensitized solar cells

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Abstract

The preparation of a novel Nb_2O_5 blocking layer deposited between fluorine-doped tin oxide (FTO) and nanocrystalline TiO_2 layer and its application for hydrophobic dye Z-907 sensitized ionic liquid-based solar cells have been studied. The Nb_2O_5 blocking layer prepared by spray pyrolysis method on FTO has been characterized by scanning electron microscope (SEM) equipped with energy dispersion X-ray analysis (EDX), transmit electron microscope (TEM), electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS). Thin Nb_2O_5 films work as a potential blocking layer between FTO and nanocrystalline TiO_2 layer in ionic liquid electrolyte cells, improving V_{oc} and finally giving a better conversion efficiency of dye-sensitized TiO_2 solar cells. Impedance spectroscopy indicates that the blocking layer can increase shunt resistance especially related with the charge transport at FTO–TiO_2/dye/ionic liquid electrolyte and decrease the series resistance to some extent by constructing the potential barrier. Analysis of diffusion coefficient and lifetime of electrons in the cells confirms that they compensate each other when the blocking layer was introduced, leading to a little influence on the diffusion length (L). The remarkable improvements of V_{oc} and fill factor for the DSCs suggest that the thin Nb_2O_5 is an effective blocking layer at FTO and TiO_2 interface, contributing to unidirectional transport of electrons in the ionic liquid-based dye-sensitized nano-TiO_2 solar cells.

Keywords: Nb_2O_5; Blocking layer; Dye-sensitized solar cell; Impedance spectroscopy

1. Introduction

Since the first successful introduction of nanocrystalline dye-sensitized solar cell (DSC) appeared in 1991 [1], great progress has been made in this domain, not only in promising sensitizers, novel kinds of electrolytes but also in multi-layered or modified electrodes. However, from the point of practical application, organic liquid electrolytes may not be a good choice because of their shortcomings such as difficulty of sealing for evaporation and instability at high temperature. Therefore, many attempts to form quasi-solid state electrolyte by using gelator [2,3], organic-capped nanoparticles [4,5] or polymers [6] and application of low molecular weight oligmer [7] as polymer electrolytes have been investigated with interesting progress. Much attention [8–11] has recently been paid to improve the performance of the ionic liquid-based DSCs because of the features of ionic liquid such as high ionic conductivity, non-volatility, improved electrochemical stability and non-flammability [12–14].

In such kinds of ionic liquid-based DSCs, which composed of a dye-adsorbed nano-TiO_2 layer, fluorine-doped tin oxide (FTO) glass anode as the window electrode, electrolytes as charge carrier and the counter electrode, unidirectional charge flow with no electron leakage at the interfaces is essential for the high energy conversion efficiency. According to the unidirectional electron transporting principle of DSCs, there are four important interfaces in the devices as shown in Fig. 1 (left). These are the interfaces of FTO/TiO_2, TiO_2/dye, dye/electrolyte (or hole transporting materials), and electrolyte/counter electrode (usually platinized FTO electrode). Such interfaces not only play an important role in the parameters of the DSCs, but also are hot topics in LED [15], silicon solar cells [16] and other photovoltaic devices [17].

In the last several years, there is a great progress in electrode modification of TiO_2 including mechanism study through introducing Nb_2O_5 [18], $SrTiO_3$ [19,20], Al_2O_3 [21] and so on [22], which mainly focuses on the decrease of the charge

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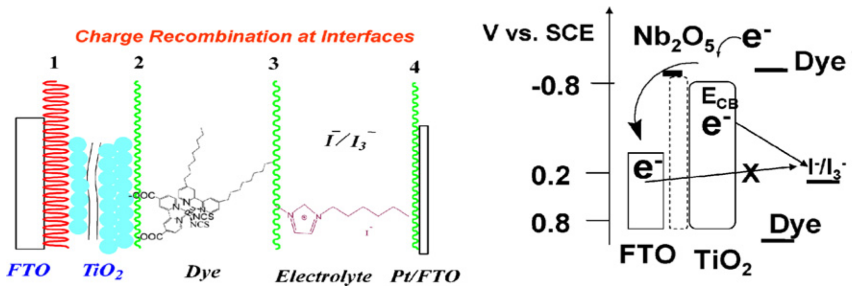

Fig. 1. Schematic view of interfaces in the DSC device and the electron transfer of the new structured electrode.

recombination at the interface of TiO_2/dye. On the other hand, other investigation on the interface of dye/electrolyte (or hole transporting materials) has been carried out through so called inter-surface engineering in solid state DSCs with self assembly method [23]. Although some groups have studied the interface of FTO/TiO_2 mainly to establish some models [24–29] of DSCs or just only characterize [30,31] and investigate its effectiveness [32–34] by employing a compact TiO_2 layer, there is no intense investigation on such important interface in DSC. That is, the electron leakage from the interface of FTO/TiO_2 has been ignored in DSC research as mentioned by Prof. L.M. Peter in his very recent articles [35–37].

Recently, we have reported using different oxides as novel blocking layers at FTO/TiO_2 interface of hydrophobic dye (Z-907) sensitized TiO_2 solar cells and found that Nb_2O_5 can be a potential blocking layer between FTO and TiO_2 nanocrystalline layers to suppress the electron leakage, resulting in an improvement of open circuit voltage (V_{oc}) with better conversion efficiency of dye-sensitized ionic liquid-based solar cells [38]. Such scheme of the electron transport is demonstrated in Fig. 1 (right). It should be noted that the blocking layer has much more effect on conversion efficiency in ionic liquid DSCs than organic liquid DSCs at 1 sun. In this article, we investigate the influence on the electron lifetime, electron diffusion coefficient and the shunt resistance after the introduction of Nb_2O_5 blocking layer in this interface. Moreover, the microstructure of FTO/Nb_2O_5 and what kind of Nb species left on FTO are investigated with full analysis to get other useful information for further understanding the usage of successful blocking layer and its limitation.

2. Experimental

2.1. Materials

N-Methyl-benzimidazole (NMBI) and I_2 were purchased from Aldrich. 4-*tert*-Butyl-pyridine was purchased from Acros. $Nb(OEt)_5$, LiI and other organic solvents were purchased from Wako Chemical Co. Imidazolium salts, i.e., 1-ethyl-3-methyl-imidazolium dicyanamide (EMIm-DCA), 1-ethyl-3-methyl-imidazolium thiocyanate (EMIm-SCN) were purchased from Sanko Chemical Co. The fluid imidazolium salt, 1-ethyl-3-methyl-imidazolium tricyanomethanide (EMIm-TCM) was a gift from Institute of Research and Innovation, Chiba, Japan.

2.2. Preparation of Nb_2O_5 blocking layer and fabrication of solar cell

The solution of $Nb(OEt)_5$ in ethanol (0.02 M) was sprayed layer-by-layer from a distance around 15 cm onto the FTO substrate whose temperature was kept over 400 °C. And the feed rate of Nb_2O_5 precursor solution was 7 ml/min under compressed air (0.1–0.2 MPa). Each next portion of the aerosol was applied after at least 30 s pause to guarantee the pyrolysis of the previous layer. The thickness of Nb_2O_5 is around 100 nm for 50 layers. Then the prepared FTO/Nb_2O_5 substrates were annealed at 500 °C for 1 h.

Nanoporous TiO_2 electrodes were prepared on a transparent conductive substrate (Nippon Sheet Glass, SnO_2:F, 10 Ω/sq) or FTO/Nb_2O_5 substrates using the colloidal Nanoxide-T paste (Solaronix) by doctor-blade techniques. The films were annealed at 450 °C for 30 min in air. The resulting TiO_2 films (thickness was around 5.5 μm, measured by a surface profiler, Sloan, Dektak3) were cut into pieces and heated again at 110 °C for 15 min, and at this temperature, the electrodes were immersed into 3.0×10^{-4} M *cis*-bis(isothiocyanato)(2,2′-bipyridyl-4,4′-dicarboxylato)(2,2′-bipyridyl-4,4′-di-nonyl) ruthenium(II) (known as Z-907, Solaronix) in acetonitrile/*tert*-butanol (1:1) for 18 h. After washed with acetonitrile, the sensitized electrode was covered with platinized conducting glass as a counter electrode. Typical areas of the electrodes were around 0.2 cm^2. The photoelectrochemical properties of the DSCs were studied by recording the current–voltage (*I–V*) characteristics of the unsealed type cell under illumination of AM1.5 (1 Sun; 100 mW/cm^2) using a solar simulator (Yamashita Denso, YSS-80). Unless specially emphasized, HMImI (1-hexyl-3-methyl-imidazolium iodide) with iodine ($[I^-]$: $[I_2]$ = 10:1) was generally used as a standard electrolyte. The IV data were all averaged for three samples.

2.3. Characterizations of electrodes

The morphologies of the substrates were observed by scanning electron microscope (SEM, S-4700, Hitachi). Microstructure of the cross-section of the FTO/Nb_2O_5/nano-TiO_2/dye and its elemental distribution analysis were obtained from FIB-STEM, HD-2300, Hitachi.

In the following experiments, cells sealed with film (HIMILAN, thickness = 30 μm, Mitsui–Dupont Polychemical) were fabricated. Electron diffusion coefficients (*D*) and electron life-