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Micro- and electronic structure optimization of Ru-doped TiO_2 electrodes for efficient dye-sensitized solar cells

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ABSTRACT

At both micro- and electronic levels, this paper investigates the effects of Ru-doping on the efficiency of TiO_2-based dye-sensitized solar cells (DSSCs). A two-layered working electrode design, one for TiO_2 (P-25) and the other for Ru-doped TiO_2, respectively with and without a p-n junction, is applied. Two calculations based on first principles thermodynamics using the computer software (FactSage) are performed to simulate the chemical equilibria of Ru-TiO_2 particles at 600 °C as well as to demonstrate the ability of Ti and Ru in taking oxygen atoms to form TiO_2 or RuO_2 at 600 °C. Our results reveal a 9.5% increase in open-circuit photovoltage (V_{oc}) as well as a 83.4% increase in short-circuit photocurrent density (J_{sc}), compared with the DSSC fabricated with a TiO_2 electrode. The observed enhancement in both V_{oc} and J_{sc} can be explained by Ru-modified defect levels in the TiO_2 band gap, which may be the origin of the improved performance. Due to the formation of a p-n junction (p-type Li-doped NiO and n-type Ru-doped TiO_2) in the working electrode, the value of V_{oc} has been further increased while maintaining a high J_{sc}. This study advances our fundamental understanding and methodology on metal-doping in general photo-electrodes.

1. Introduction

Low-cost dye-sensitized solar cells (DSSCs) can be manufactured using a variety of substrates with very little effect on the environment (Lewis, 2007; O'Regan and Grätzel, 1991; Caramori et al., 2010; Kim et al., 2008). The power conversion efficiency (η) of DSSCs is determined by the short-circuit photocurrent density (J_{sc}) and open-circuit voltage (V_{oc}). The former is related to light absorption characteristics, whereas the latter is related to electron-hole recombination (Wang et al., 2004).

The dependence of J_{sc} values on light absorption has prompted the development of methods to improve light capturing performance, such as the inclusion of light-scattering layers within the working electrode (Yang and Leung, 2011; Chou et al., 2012a; Hore et al., 2006; Ito et al., 2008; Jeng et al., 2013; Lan et al., 2011; Lee et al., 2009; Liu et al., 2012; Tu et al., 2012; Wang et al., 2004). V_{oc} can be increased by inserting a wide band semiconductor (such as ZnO) (Chou et al., 2012b, 2012c; Guo et al., 2012) and/or a semiconducting p-n junction (such as TiO_2/NiO) (Bandara et al., 2005; Chou et al., 2011, 2014a) between the electrode and dye. However, increasing the photocurrent by extending the retention period of light in a DSSC can also increase electron recombination in the dye (or electrolyte). In contrast, increasing V_{oc} through the introduction of an energy barrier or p-n junction can lead to a decrease in J_{sc} resulting from an increase in electrical resistivity. Nonetheless, a number of researchers have succeeded in enhancing V_{oc} as well as J_{sc} simultaneously. For example, a light-scattering layer of Ni-doped TiO_2 particles was proposed in (Chou et al., 2014a) and a Li-doped NiO electrode was proposed in (Chou et al., 2014b). In this study, we sought to further the development of a multi-functional working electrode with increased J_{sc} as well as V_{oc}.

Researcher have recently reported on the use of titanium dioxide doped with a single type of metal-ion, such as Ru-TiO_2, in order to produce a red shift in the photo-physical response of TiO_2 (Choi et al., 2010) and thereby enhance photo-catalytic through the introduction of a Schottky barrier (Sasirekha et al., 2006). However,

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very little research has focused on the use of Ru-TiO_2 in the working electrode of DSSCs as a means of enhancing the light harvesting efficiency, and the role played by Ru in the electronic structure of TiO_2 has yet to be fully elucidated. A number of researchers have reported that Ru doping decreases the band gap (Houskova et al., 2009); however, Kong et al. (2015) reported that Ru-doping can actually increase the band gap of TiO_2. To further increase V_{oc}, we applied a p-n junction structure in order to prevent electron-hole recombination. Furthermore, little attention has been paid to the use of Ru-TiO_2 + $Li_xNi_{1-x}O$ composite particles in the working electrode to produce a p-n junction and enhance light harvesting efficiency.

This paper proposes a novel multi-functional electrode comprising TiO_2 (P-25) + Ru-TiO_2 + $Li_{0.01}Ni_{0.99}O$ composite particles, which function as a p-n junction in the working electrode of a DSSC (Fig. 1). The proposed Ru-doped hybrid electrode was shown to increase the absorption of light in the visible region. A sol-gel method was used in the preparation of TiO_2 (sol-gel), Ru-TiO_2, and $Li_{0.01}Ni_{0.99}O$ particles, whereas wet ball-mill-mixing was used to prepare composite particles of TiO_2 (P-25) + TiO_2 (sol-gel), TiO_2 (P-25) + Ru-TiO_2, and TiO_2 (P-25) + Ru-TiO_2 + $Li_{0.01}Ni_{0.99}O$. This study investigated the degree to which the η of DSSCs is influenced by quantity of Ru in Ru-TiO_2, the mass ratio of TiO_2 (P-25) to Ru-TiO_2, and the mass ratio of TiO_2 (P-25), Ru-TiO_2, and $Li_{0.01}Ni_{0.99}O$. We also compared a conventional DSSC with TiO_2 (P-25) electrode and the DSSC fabricated using the proposed working electrode.

2. Experiment details

2.1. TiO_2 (P-25) + Ru-TiO_2 + $Li_{0.01}Ni_{0.99}O$ composite particles

The methods used to produce TiO_2 (sol-gel), Ru-TiO_2, and $Li_{0.01}Ni_{0.99}O$ particles using the sol-gel method are detailed in our previous works (Chou et al., 2012a, 2014b). The parameter values of the precursor solution and solute are listed in Table 1. Calcination was performed at temperatures of 600 °C to obtain TiO_2 (sol-gel) (or Ru-TiO_2) and at 730 °C to obtain $Li_{0.01}Ni_{0.99}O$. The TiO_2 was doped with Ru at 0.1 wt%, 0.2 wt%, and 0.3 wt%. Titanium dioxide particles (TiO_2, Uniregion Biotech P-25) (20% rutile and 80% anatase) with an average particle size of 21 nm were mixed with TiO_2 (sol-gel), Ru-TiO_2, and/or $Li_{0.01}Ni_{0.99}O$ to prepare TiO_2 (P-25) + TiO_2 (sol-gel), TiO_2 (P-25) + Ru-TiO_2, and TiO_2 (P-25) + Ru-TiO_2 + $Li_{0.01}Ni_{0.99}O$ composite particles using wet ball-mill-mixing. The composite particles were prepared via wet mixing with a rotor speed of 300 rpm over a period of 10 h using the mixing mass ratios listed in Table 2. Besides sol-gel method, a number of new techniques, such as incipient wet impregnation method (Sasirekha et al., 2006), impregnation method (Hamzah et al., 2012), impregnation–reduction method (Lin et al., 2014), and sonochemical method (Singh and Madras, 2016) were used in the preparation of Ru-doped TiO_2 particles.

A digital camera (Panasonic DMC-LZ2) and a scanning electron microscope (SEM) (HITACHI, 600-S) were respectively used to obtain photographs and SEM micrographs of TiO_2 (sol-gel), Ru-TiO_2, and $Li_{0.01}Ni_{0.99}O$ particles and composite particles of TiO_2 (P-25) + Ru-TiO_2 + $Li_{0.01}Ni_{0.99}O$. A powder X-ray diffractometer (Shimadzu, XRD-6000) was used to characterize the TiO_2 (sol-gel) and Ru-TiO_2 particles and TiO_2 (P-25) + Ru-TiO_2 + $Li_{0.01}Ni_{0.99}O$ composite particles. A dynamic light-scattering particle size analyzer (HORIBA, LB-550) was used to determine the average sizes of TiO_2 (sol-gel), Ru-TiO_2, and $Li_{0.01}Ni_{0.99}O$ particles. A UV–vis-NIR spectrophotometer (Jasco, V-600) was used to determine the absorbance values of TiO_2 (sol-gel) and Ru-TiO_2 particles and calculate their band gaps in accordance with the Tauc-Sunds equation (Cao et al., 2013).

In addition, two calculations based on first principles thermodynamics using FactSage (Balea et al., 2009) were performed as follows: (1) to simulate the chemical equilibria of Ru-TiO_2 particles in Test A4 at a calcination temperature of 600 °C; and (2) to demonstrate the ability of Ti and Ru in taking oxygen atoms to form TiO_2 or RuO_2 at 600 °C. The detailed calculations are discussed in Section 3.1.

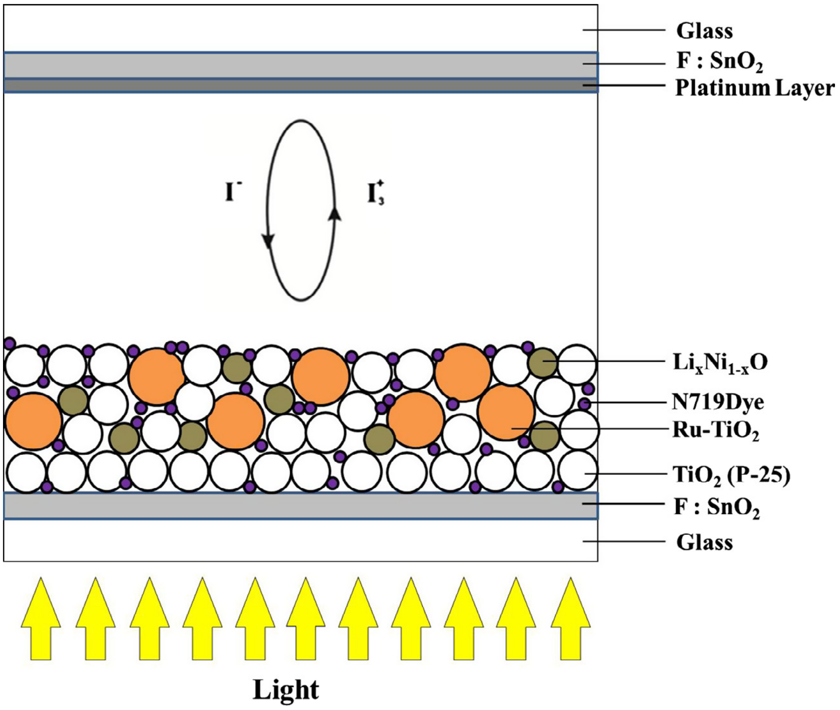

Fig. 1. Schematic of the DSSC comprising TiO_2 (P-25) + Ru-TiO_2 + $Li_xNi_{1-x}O$ composite particles.