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Effect of different trap states on the electron transport of photoanodes in dye sensitized solar cells

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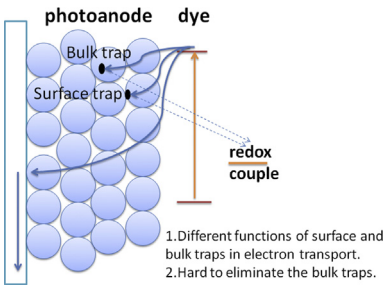
HIGHLIGHTS

- Surface traps and bulk traps in the photoanodes of DSSCs are distinguished in this work.
- The influence of each trap state to the electron transport is characterized.
- Bulk trap states should be avoided during photoanode preparation to get high quality DSSCs.
- Interface recombination time is closely related to the property of the trap states.

GRAPHICAL ABSTRACT



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ABSTRACT

Trap states play important role in electron transport of dye sensitized solar cells (DSSCs). Different trap states (surface and bulk traps) contribute differently to the performance of DSSCs. However, there is a lack of classification of the trap states, especially in recent doping works of the photoanodes. In this work, the Ce^{4+} (0.3, 0.6 and 0.9% molar ratio) in TiO_2 and Ti^{4+} (15, 40 and 70% molar ratio) in SnO_2 are assigned to surface traps and surface-and-bulk coexisted traps, respectively. The property of each trap state and its influence to the electron transport are characterized. Both the surface and bulk traps deteriorate the electron transport in DSSCs, however, the negative role of surface traps can easily be eliminated by surface modification in contrast to the bulk traps. Furthermore, contrary to the literature that the trap states will accelerate the interface recombination, it is found that the interface electron recombination time is prolonged with Ce^{4+} surface traps in TiO_2 and Ti^{4+} bulk traps in SnO_2, indicating that the recombination time is closely related to the property of the trap states.

1. Introduction

Photoelectrochemical DSSC is attracting more and more attention due to its low cost and improving efficiency [1–3]. As an important part in DSSCs, porous wide-band gap semiconductor photoanodes take part in accepting and transporting the electrons from the adsorbed dye molecules [4]. Therefore, the electronic structure of the semiconductors (the conduction band potential, the trap states distribution) largely influences the electron transport in the porous electrode and the electron recombination process from photoanode to the redox couple. In order to tailor the property of the photoanode, several methods have been developed, one of which is the surface modification of a layer of wide band gap metal oxide, such as $SrTiO_3$ [5], MgO [6], ZnO [7] and Nb_2O_5 [8] on the porous photoanode. The purpose is to bring up the conduction band to negative potential and diminishment of the surface trap states and the interface recombination. The photovoltage is thus

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usually improved by this method. Another method is doping metal or non-metal atom into photoanodes to tailor their property. It has been reported intensively that many positive effects have been achieved by doping to improve the performance of photoanode in DSSCs. Nb^{5+} (< 2% molar content) doping in TiO_2 effectively controlled the surface states, thus it facilitated the electron transport in TiO_2 photoanode [9,10]. W^{6+} doping in TiO_2 (within a 0.1–2% content) brought down the conduction band potential of photoanode, thus enlarged the driving force of the electron injection from the dye into the photoanode [11]. Zn^{2+} (< 0.7% content) doping in TiO_2 reduced the trap states of the nanocrystalline, which lead to the improvement of the electron transport [12]. It is noticed that the performance of the DSSCs does increase at a certain percentage of doping. However, it usually turns to decrease noticeably at higher doping amount with the reason unspecified or simply ascribed to the induced trap states which impede the electron transport. Though the negative role of the excessive trap states is assured, the type of trap states (whether it is a bulk or a surface trap state) and the effect of each trap states on the electron transport have not been discussed yet in the previous doping works.

The electron transport in photoanodes of DSSCs can be regarded as a trap–detrap electron diffusion process [13]. The trap states of pure nanocrystalline photoanode are mainly composed of surface trap states, because of the large surface area of the nanoporous films [14,15]. However, when a third element is doped in the nanocrystalline, it is prone to reside in the particle (substitute the lattice atoms or stay interstitial in the lattice) or on the surface of the nanocrystalline, thus forming bulk and surface trap states, respectively. Both the surface and bulk trap states influence the electron transport in DSSCs, while the surface states are usually considered as the interface recombination centers [14–17]. It is quite important to distinguish the surface trap states from bulk trap states in doping works, because they contribute differently to the electron transport of the photoanode and the methods to eliminate the trap states may be differed from each the other either. In our previous work, Ce^{4+} doped TiO_2 and Ti^{4+} incorporated SnO_2 photoanodes are prepared for DSSCs [18,19]. The performances of the DSSCs decrease at high amount of the added elements which is due to the excessive trap states formed. In this work, a comparison is carried out between Ce^{4+} doped TiO_2 photoanode and Ti^{4+} incorporated SnO_2 photoanode: the lattice structure and the chemical bonding of the nanocrystallines change differently with the third element amount increase, and the performances of the DSSCs respond differently with $TiCl_4$ surface treating of the electrode. According to the phenomenon, the type of trap states in Ce^{4+} doped TiO_2 and Ti^{4+} incorporated SnO_2 is assigned to surface traps and surface-and-bulk coexisted traps, respectively. The role of each trap states on the electron transport in the photoanodes and the special property of the trap states in the interface recombination process are discussed. It is suggested from the electron transport analysis that bulk trap states should be avoided during photoanode preparation to get high quality photoanodes of DSSCs.

2. Experimental section

2.1. Preparation of the photoanodes and DSSCs

Ce^{4+} doped TiO_2 and Ti^{4+} incorporated SnO_2 were prepared according to the literature [18,19]. The contents we discussed here were 0.3, 0.6 and 0.9% of Ce^{4+} doping, which were marked as Ce-03, Ce-06 and Ce-09, respectively; and 15, 40 and 70% of Ti^{4+} incorporated SnO_2 were marked as T15, T40 and T70 respectively. The photoanodes were prepared by screen printing the paste. After annealing at 500 °C for 30 min, the 0.25 cm^2 photoanodes were obtained. For $TiCl_4$ treatment, the photoanodes were immersed in $TiCl_4$ aqueous solution (40 mM) for 30 min at 70 °C. After washing by pure water and ethanol twice, the photoanodes suffered thermal treatment at 500 °C for 15 min again.

The prepared photoanodes were immersed in dye N719 solution (0.3 mM in acetonitrile and tertbutyl alcohol with volume ratio of 1:1) over night. The photoanode was sealed with Pt counter electrode by Surlyn films. The electrolyte (0.6 M methylpropylimidazolium iodide, 0.05 M I_2, and 0.1 M LiI in acetonitrile with tert-butyl pyridine) was back filled in the cell.

2.2. Characterization of the photoanodes

The X-ray diffraction (XRD, 20–60°) was performed by Rint-2500 diffractometer (Rigaku, Japan) with Cu Kα radiation operated at 40 kV and 300 mA. The incorporation of the elements in nanocrystal was examined by X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM, Japan) using Al Kα radiation. The cyclic voltammetry (*CV*) was performed with the three electrodes system, using Pt wire as counter electrode, saturated calomel electrode (SCE) as reference electrode and the photoanode (thickness: 5 μm and area of 0.25 cm^2) as working electrode. 0.1 M $TBAPF_6$ (Tetrabutylammonium hexafluorophosphate) in acetonitrile was served as the supporting electrolyte.

2.3. *I–V* curves of the DSSCs and photoelectrochemical measurements

I–V curves of the DSSCs (active area of 0.2304 cm^2 by a black mask) were measured with a digital source meter (Keithley2400) under simulated solar illumination at 1 Sun, AM1.5 (Wacom, Japan). The intensity modulated photocurrent spectroscopy (IMPS) measurements were carried out on electrochemical work station (Solartron 1287 and 1255B) with two-electrode system under a series of light illumination (provided by 446 nm laser). The open circuit voltage decay (OCVD) spectra were also recorded by electrochemical work station after the simulated sunlight was turned off.

3. Results and discussions

3.1. Crystallinity change of the photoanodes by doping

Fig. 1 is the XRD patterns of Ce^{4+} doped TiO_2 and Ti^{4+} incorporated SnO_2 nanoparticles. Contrary to the similar peak position of Ce^{4+} doped TiO_2 photoanodes, the position of the diffraction

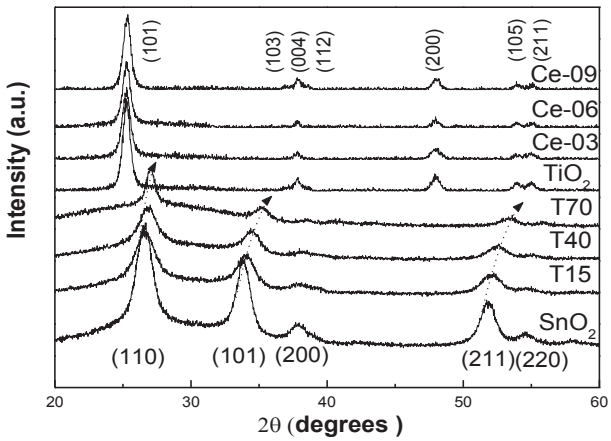

Fig. 1. XRD patterns of Ce^{4+} doped TiO_2 and Ti^{4+} incorporated SnO_2 photoanodes.