Electrochimica Acta 232 (2017) 38–43

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

An Investigation of Surface States Energy Distribution and Band Edge Shifts in Solar Cells Based on TiO_2 Submicrospheres and Nanoparticles

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A R T I C L E   I N F O

Article history:
Received 21 October 2016
Received in revised form 24 January 2017
Accepted 21 February 2017
Available online 22 February 2017

Keywords:
surface states
TiO_2 submicrospheres
dye-sensitized solar cells (DSSCs)
electrochemical impedance spectroscopy (EIS)
electron transport

A B S T R A C T

TiO_2 submicrospheres were often used as photoanodes in dye-sensitized solar cells (DSSCs) due to the high internal surface area and great scattering properties. However, surface states in TiO_2 submicrospheres limit the electron transport process. In this paper, an investigation of surface states in TiO_2 submicrospheres and traditional TiO_2 nanoparticles was conducted by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The chemical capacitance, electron transport resistance and recombination resistance were interpreted in a consistent framework. The electron transport and recombination behavior were also studied by open-circuit voltage decay measurements (OCVD) and intensity-modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS). The results show that the TiO_2 submicrospheres based films possess a larger number of surface states and a shallow energy distribution than TiO_2 nanoparticles under the same film thickness. Furthermore, the fitted data indicate that the electron transport in TiO_2 submicrospheres film was faster than in traditional nanoparticles film owing to their high electron concentration and shallow surface states energy distribution. The discussion highlights the location of surface states in the band gap region of TiO_2 film, which plays an important role in electron transport and charge recombination in DSSCs.

1. Introduction

In recent years, TiO_2 submicrospheres have often been used in photovoltaics because of their high internal surface area and great scattering properties [1–3]. Such as, TiO_2 submicrospheres was used as the scattering layer in DSSCs to improve the light harvesting by Gratzel et al. [3]. Caruso and co-workers have found that 550 ± 50 nm submicrospheres possess the highest light scattering and 320 ± 50 nm submicrospheres own the highest dye adsorption [4]. Additionally, Huang et al. have also used the TiO_2 submicrospheres as the scaffold layer for efficient mesocopic perovskite solar cells [5]. It is believed that TiO_2 submicrospheres are one of the ideal nanomaterials for high efficiency solar cells.

However, the high specific surface area of TiO_2 submicrospheres inevitably leads to a large number of surface states in the mid-gap region, which would influence the electron transport in TiO_2 network directly (When the electrons inject into the conduction band, most of them would be trapped at the surface states) [6,7]. Meanwhile, several papers have studied the surface states in traditional TiO_2 nanoparticle based films, and put forward a lot of models to explain the electron transport and recombination behavior. Juan Bisquert and co-workers have used the multiple trapping model (MT) to illustrate the charge transfer process [6]. Nelson et al. have proposed the continuous-time random walk model to explain the electron transport in nanocrystalline TiO_2 films [8]. In order to study the influence of surface states on the electron transport process, lots of methods have been proposed [9–12], such as, cyclic voltammetry (CV), open-circuit voltage decay (OCVD) measurements, intensity-modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS) and electrochemical

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http://dx.doi.org/10.1016/j.electacta.2017.02.121
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impedance spectroscopy (EIS). Numerous studies have been published about the traditional TiO_2 particle's surface states [13–16]. Although obvious improvements of the efficiency were obtained by adopting submicrospheres as photoanode in DSSCs, the surface states of TiO_2 submicrospheres are still to be investigated in details.

In this paper, TiO_2 submicrospheres were successfully synthesized by a two-step method. The surface states energy distribution, band edge shifts, electron transport resistance and recombination resistance of the TiO_2 submicrospheres and traditional particle were investigated. By comparing the location of surface states and the electron transfer kinetics, we investigate the influence of the surface states on the electron transport and recombination behavior. This work explain the excellent performance of the TiO_2 submicrospheres from the aspects of surface states, and exhibit the detail working mechanism of surface states on the electron transfer kinetics.

2. Experimental Section

2.1. Preparation of TiO_2 submicrospheres

The TiO_2 submicrospheres (500 nm in diameter) were synthesized as described in our previous work [2]. In order to crystallize the TiO_2 submicrospheres, the as-product was re-dispersed to a mixed solvent containing ethanol (40 mL), distilled water (20 mL) and ammonia solution (2 mL, 28 wt.%). Under vigorous stirring at room temperature for 30 min, the mixture was transferred into a telflon-line autoclave (100 mL) and heated at 160 °C for 16 h. The products were obtained by centrifugation (4500 rpm) and by washing three times with absolute ethanol.

2.2. Fabrication of dye-sensitized solar cells

The TiO_2 submicrospheres powder (4.8 g) was mixed with α-terpineol (19.2 g) and ethyl cellulose (9.6 g) to form the viscous paste [2]. Then the paste was screen-printed onto FTO glass and sintered in air at 510 °C for 30 min. The thickness of the films (5 mm × 5 mm) was about 7 μm determined by surface profilometer (XP-2, AMBIOS Technology Inc., USA). After cooling down, the films were immersed in a dye solution containing **C101** (Dyesol) (300 μM Ru-based heteroleptic complex Na-*cis*-Ru(4,4′-(5-hexyltiophen-2-yl)-2,2′-bipyridine)(4-carboxylic-acid-4′-carboxylate-2,2′-bipyridine)(thiocyanate)$_2$) with cheno-3a, 7adihydroxy-5b-cholic acid (**CDCA**) (Sigma-Aldrich) at room temperature for 12 h. Before cell construction, these films were washed with acetonitrile. The sensitized photoanodes were assembled with a Pt-modified counter electrode and electrolyte (30 mM I_2, 50 mM LiI, 1 M 1, 3-dimethylimidazolium iodide (DMII), 0.5 M tertbutylpyridine, and 0.1 M guanidinium thiocyanate (GuSCN) in a solvent mixture of 85% acetonitrile with 15% valeronitrile) by a laser engraved 60 μm Surlyn gasket under heat and pressure. As a comparison, a TiO_2 nanocrystalline sample composed of roughly 20 nm nanoparticles (Dyesol, denoted NP-20) was also fabricated. The cell was masked by a black tape with a 5 × 5 mm^2 aperture before measurements, and the area of the cell was 0.25 cm^{-2}.

2.3. Characterizations

The morphology of TiO_2 submicrospheres was investigated by a scanning electron microscopy (SEM) (S-4800, HITACHI, Japan). The current density-voltage (*J-V*) measurements were carried out on a Keithley model 2420 digital source meter controlled by Test point software under a xenon lamp (100 mW cm^{-2}).

All the following electrochemical measurements were carried out at 25 °C. Cyclic voltammetry (CV) was done in a standard three-electrode cell using a Hg/HgCl (0.1 M $LiClO_4$) reference electrode and a Pt counter electrode. Electrochemical Impedance Spectra (EIS) were recorded by a computer controlled potentiostat (Autolab 320, Metrohm, Switzerland) in a frequency range of 10 mHz to 1 MHz applied in the dark. Intensity-modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS) measurements were performed on IM6e workstation using light-emitting diodes (λ= 610 nm) driven by Xpot (Germany, Zahner). The LED provided both dc and ac illumination components, the amplitude of the modulated component was 10% or less of dc component, and the frequency range was 3 kHz to 0.1 Hz. Open-circuit voltage decay (OCVD) measurements were carried out on an IM6e electrochemical workstation using light-emitting diodes (λ = 610 nm) driven by Xpot (Germany, Zahner).

3. Results and Discussion

3.1. Characterization

The morphology and XRD-patterns of the TiO_2 submicrospheres (denoted TiO_2 MS) are shown in Fig. S1. The TiO_2 MS have an interconnected three-dimension structure and are composed of nanosized TiO_2 particles. The crystallite size estimated from the full width at half maximum of the (101) peak (most intense peak) was 20.70 nm according to the Scherrer equation [2]. Moreover, specific surface area (Brunauer-Emmett-Teller, BET) of the TiO_2 MS was investigated by nitrogen adsorption-desorption. As shown in Fig. S2, the specific surface area for the TiO_2 MS was $104.0 \pm 4.6\ m^2\ g^{-1}$, which was much higher than that of NP-20 ($75.9\ m^2\ g^{-1}$).

CV is an effective method that can give information about the total number of surface states in nanocrystalline electrodes [17,18]. As shown in Fig. 1, the two sample's CV curves exhibit a similar shape. The electrons would inject into surface states under forward bias, forming a capacitive current in the forward scan. For the reverse scans, the current was closed to zero at the more positive potentials, indicating regeneration of surface states and recovery of the injected negative charge [19,20]. It was mentioned that the anodic peak current was proportional to the scan rate (Eq. (1)). In this work, 500 mV s^{-1} was chosen as the potential scan rate. The potential was scanned from −1.2 V to 0.8 V. The anodic peak could give information about the surface states of TiO_2 films. Under the same film thickness, TiO_2 MS have more number of surface states than NP-20, which might be ascribed to the higher surface area of

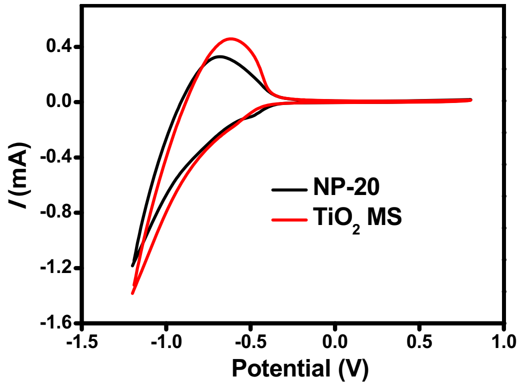

Fig. 1. Cyclic voltammograms for NP-20 and TiO_2 MS based films. The measurements were performed in the dark and at 25° C. The scan rate is 500 mV s^{-1}.