

TiO₂ photoanode surface modification via combined action of samarium and titanium salt in dye-sensitized solar cells



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ABSTRACT

Mesoporous TiO₂ films were modified with Sm(NO₃)₃·6H₂O and TiCl₄ mixture solution in dye-sensitized solar cells. Samarium oxide was formed after modification according to UV–vis absorption spectra and X-ray photoelectron spectra (XPS) analyses, and acted as energy barrier on TiO₂ surface. The electron recombination reaction with I₃⁻ can be suppressed when samples are treated using Sm³⁺/TiCl₄ solutions via electrochemical impedance spectroscopy (EIS) and open circuit voltage decay (OCVD) analyses. With the mesoporous TiO₂ film modified by the TiCl₄ mixture solution contained 0.07 M samarium trinitrate, the power conversion efficiency of the dye-sensitized solar cell is increased from 6.91% to 8.23%. The enhanced performance is ascribed to the increase of dye loading, the reduce of surface state density, and the energy barrier created on TiO₂ surface. It is a effective method to improve the power conversion efficiency without requiring a tedious synthesis pathway.

1. Introduction

Dye-sensitized solar cells (DSSCs) is potentially one of most important energy-conversion devices, because of its low production cost and non-toxic assembly process [1,2]. The working principle of DSSCs is significantly different from conventional silicon solar cell. The dye molecules which loaded on photoanode absorb photons and convert them to charges without occurring of intermolecular transport of electronic excitation. After separation of holes and electrons, the holes move towards the counter electrode (CE) by means of the diffusion of iodide/tri-iodide (I⁻ / I₃⁻) redox, while electrons are injected into the conduction band of TiO₂ and then transport to the conductive substrate [3]. However, the recombination occurring to TiO₂ particle and the uncovered FTO surfaces greatly reduced the power conversion efficiency (PCE). Moreover, the insufficient connectivity between TiO₂ particles produces the similar result, because of the increase of electron transfer length and resistance. Those are considered as the obstacles to achieve a higher power conversion efficiency [4–6]. Therefore, the optimization of DSSCs will be a long-term challenge.

It is widely acknowledged that the traps resulting from electronic states below band gap of TiO₂ act as recombination centers [7]. Tremendous efforts have been made to reduce the electron recombination. Surface treatment is an usual modification method to enhance solar-to-electrical energy conversion efficiency of DSSCs by controlling the transport and recombination of photoelectrons. As the most usual

modification method, TiCl₄ treatment can increase the surface area of TiO₂ nanocrystalline films to load more dyes, adjust the TiO₂ conduction band edge position and reduce the density of surface traps to suppress the electron recombination process [8]. Moreover, porous TiO₂ modified with an insulating layer or a wide band gap semiconductor layer, such as MgO [9], MgTiO₃ [10], Al₂O₃ [11,12], CaCO₃ [13], ZnO [14], Nb₂O₅ [15], La₂O₃ [16], Sm₂O₃ [17], create an energy barrier layer to suppress the recombination, which has been shown the enhanced performance of the DSSCs. It can be also observed that PCE of DSSCs is increased significantly, which the mesoporous TiO₂ electrodes were modified with collaborative modification treatment methods, such as lanthanum acetate and TiCl₄ mixed solution [18], TiCl₄ and Nb(OEt)₅ mixed solution [19], TiCl₄ and AlCl₃ mixed solution [20], compared with TiCl₄ treatment method. In our previous work, the PCE was increased by 18.67% when the porous TiO₂ electrodes were modified using ZrCl₄ and TiCl₄ co-modification compared to the TiCl₄ treatment alone [21].

In this work, we proposed to increase the photocurrent and photovoltage using Sm³⁺/TiCl₄ collaborative treatment of mesoporous TiO₂ electrodes. We have investigated the performance of DSSCs which modified using different Sm(NO₃)₃ concentrations with constant TiCl₄ concentrations.

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2. Material and methods

2.1. $\text{Sm}^{3+}/\text{TiCl}_4$ collaborative modification treatment of TiO_2 film

TiO_2 paste and compact layer on FTO glass (15 Ω /square, Nippon Sheet Glass, Japan) were prepared as previously reported [22]. Mesoporous TiO_2 films were deposited by the doctor blade method onto pretreatment FTO glass. After drying at 60 °C for 60 min, the films were sintered at 325 °C for 5 min, at 375 °C for 5 min, and at 450 °C for 15 min, and finally, at 500 °C for 15 min. The modified solutions were prepared by dissolving different quantity of samarium nitrate hexahydrate (> 99.9%) into 40 mM TiCl_4 solution. The mesoporous TiO_2 films were dipped into the mixture solutions at 90 °C for 30 min. The samples, modified using different precursor solutions comprising 0.04 M TiCl_4 and different concentrations of $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, i.e., 0.01 M, 0.03 M, 0.05 M, 0.07 M and 0.1 M, were defined as STM1, STM2, STM3, STM4, and STM5, respectively. And the sample modified using 0.04 M TiCl_4 solution was defined as the control film. Subsequently, the films were washed with deionized water and ethanol and annealed at 500 °C in a muffle furnace for 30 min.

2.2. DSSCs assembly

The as-prepared films were immersed into N719 dye solution (solarix, 0.3 mM in ethanol solution) at 40 °C for 24 h. The dye-sensitized films were washed with ethanol and dried in an oven at 40 °C. The liquid electrolyte is a commercial high-efficiency electrolyte system (yingkou China, OPV tech new Energy Co, OPV-AN-I), which comprised LiI , I_2 , 4-*tert*-butylpyridine (TBP) and guanidine isothiocyanate (GuSCN) in acetonitrile. The platinum counter electrode (CE) was a commercial product prepared by magnetron sputtering. Then the I^-/I_3^- electrolyte was added into the gap between the electrodes by an injector.

2.3. Characterization

The crystal structures of the samples was characterized by X-ray diffraction (XRD, DX-1000, Dandong) with $\text{Cu K}\alpha$ radiation ($\lambda=0.15406$ nm) at a scanning rate of 4°/min. The morphology of the film and elements measurement were investigated using a field emission scanning electron microscopy (FESEM, JSM-7500F, JEOL), where the system was connected to an energy dispersive X-ray spectroscopy (EDX) detector. X-ray photoelectron spectra (XPS) were recorded with a Kratos XSAM800 spectrometer using monochromatic Al-K α radiation. The UV–vis absorption spectra of the films was measured using an UV–vis–NIR spectrophotometer (UV-1700, SHIMADZU). The current–voltage characteristic was recorded using an electrochemical workstation under a simulated solar spectrum (AM1.5) provided by a solar simulator (CEL-S500, Beijing of China). The electrochemical impedance spectroscopy (EIS) was also performed on the same electrochemical workstation in the dark at forward bias of near open-circuit voltage with the frequency ranged from 100 mHz to 100 kHz. Open circuit voltage decay (OCVD) experiment was conducted by monitoring the subsequent decay of V_{oc} after cutting off the illumination on DSSCs under open-circuit condition. The monochromatic incident photon-to-electron conversion efficiency (IPCE, Bentham, Inc.) was measured using an IPCE system (PVE 300) from 300 to 800 nm. The active area of the solar cells was controlled to 0.25 cm^2 using a mask.

3. Results and discussion

3.1. Structure and morphology properties

Fig. 1 shows the SEM images and EDX spectrogram of the control film and STM4 film. Fig. 1(a) exhibits a typical mesoporous structure, where TiO_2 nanoparticles are randomly packed with evenly distributed porosity. Estimating from the ruler, pore size of the film is about 40 ~ 60 nm. The film which modified with 0.07 M $\text{Sm}^{3+}/\text{TiCl}_4$ solution

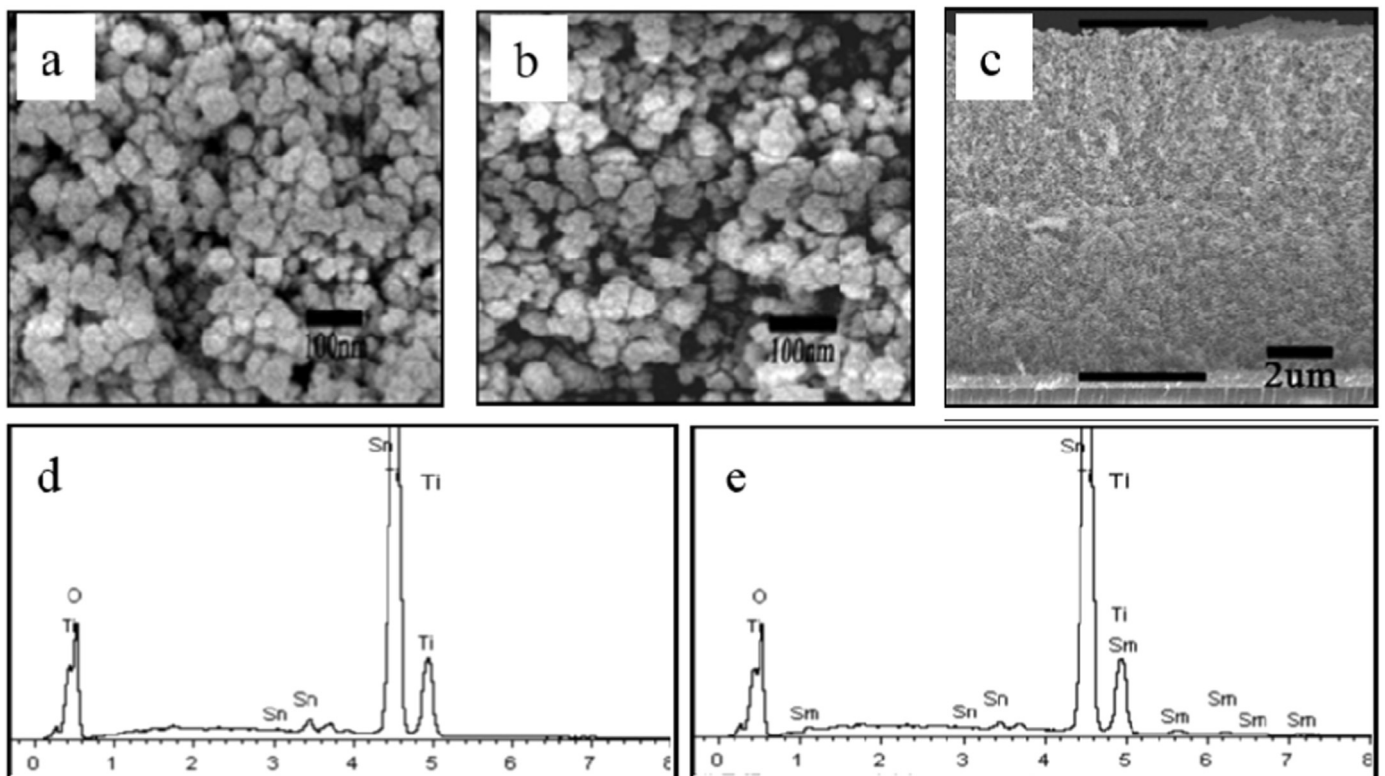


Fig. 1. Top view of SEM images of (a) the control film, (b) the STM4 film; (c) cross-sectional SEM image of the STM4 film; EDX spectrum of (d) the control film (e) the STM4 film.

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