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Effects of modified TiO_2 photoanode on the photoelectrochemical properties of dye sensitized solar cells

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ABSTRACT

The study of nanoporous TiO_2 electrodes modified by magnesium and manganese acetates in dye sensitized solar cells was reported. The formation and composition of modified electrodes were characterized by X-ray photoelectron spectroscopy and X-ray diffraction, revealing that MgO and Mn(OH)O were formed after magnesium acetate and manganese acetate treatments. Sunlight absorbance was also enhanced after such modification as supported by UV–vis spectra. The effects of modification include the increase of the dye adsorption, open-circuit voltage, short-circuit current density, and photoelectric conversion efficiency of the fabricated devices. The mechanisms of electron transfer, charge recombination, and electron lifetime were investigated by dark current and electrochemical impedance spectroscopy.

1. Introduction

During the past decades, dye sensitized solar cells (DSSCs) have attracted considerable attention because of their low-cost and ease of fabrication as compared to commercially available such as silicon-based photovoltaic devices. The energy conversion efficiency of DSSCs as high as 12.3% [1] has been achieved under AM 1.5 simulated solar light. Apart from the search for more efficient and stable dyes, modification of photoanodes has also attracted great attention. Several research groups have reported that interfacial modification of nanoporous TiO_2 films with oxide coating layer such as Al_2O_3 [2], $BaCO_3$ [3], $CaCO_3$ [4], $MgCO_3$ [5], Fe_2O_3 [6] and $CaTiO_3$ [7] can improve the photovoltaic performance of DSSCs. The effect of surface-modified TiO_2 photoanode includes the following aspects: Firstly, modification significantly increases the dye chemical adsorption on oxide surface resulting from the fact that the modified photoanode surface is more basic than bare TiO_2, and that the Brunauer–Emmett–Teller surface area is increased. The improved dye chemical adsorption causes increased concentration of free electrons in the conduction band of TiO_2. Secondly, an energy barrier is formed at the TiO_2/dye interface allowing the electron injection but hindering the charge recombination [5]. The barrier causes a reduction of the charge recombination rate and thus extending their life time in the electrode. At the same time, the barrier also reduces the back electron transfer. Lastly, the lower conduction band (CB) materials prevented electron trapping effects in the CB of TiO_2. It was very helpful to prohibit the recombination of electrons in the CB of TiO_2.

Park [5] has reported that when the TiO_2 photoelectrodes were dipped into the magnesium carbonate and acetic acid solutions without calcination, the fabricated DSSC exhibited an 8.48% efficiency which was about 16.6% higher than that of reference device with bare TiO_2 (7.27%). In this study, first we incorporated magnesium acetate onto the TiO_2 layer via dip coating process coupled with calcination to form magnesium oxide coating layer, and the resulting electrodes served as the photoanodes of DSSCs. The energy conversion efficiency of such modified DSSC was 5.3%, which was 68.3% higher than that of the reference device with bare TiO_2 (3.15%). For comparison purposes, manganese acetate was also introduced into the pores of TiO_2 layer to investigate the effects of the surface treatment on the performance of DSSCs. The results show that such modifications on the surface of TiO_2 form an energy barrier against the electron-hole recombination and increase the dye adsorption, resulting in an increase in open-circuit voltage (Voc) and short-circuit current density (Jsc) due to the increased electron lifetime and more electron injection.

2. Experimental details

2.1. Materials and solutions

Titanium(IV) isopropoxide, alpha-terpineol, and ethyl cellulose were purchased from Acros for the preparation of the TiO_2 colloids. Analytical reagent grade $Mg(CH_3COO)_2$, $Mn(CH_3COO)_2$, and $TiCl_4$ were

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purchased from Shanghai or Beijing Reagent Co.. Commercial N719 (Ruthenium 535-bis TBA; Solaronix) dye was employed as oxide semiconductor sensitizer, tert-butyl alcohol and acetonitrile purchased from Shanghai Reagent Co. were selected as solvents and distilled by molecular sieves before use. The electrolyte is composed of 4 mmol/L 1,3-dimethylimidazolium iodide, 0.6 mmol/L iodine, 2 mmol/L N-methyl- benzimidazole, 0.4 mmol/L guanidine throcyanate in 3-methoxypropionitrole, all of the chemicals were purchased from Shanghai Reagent Co. except 3-methoxypropionitrole which was purchased from Acros and distilled over CaH_2 before use. The Pt source was from H_2PtCl_6 (≥47.0%) which was purchased from KaiDa.

2.2. Preparation of the dye sensitized nanoporous electrodes and devices

The preparation of nanoporous TiO_2 colloids and the electrode fabrication were carried out following the reference [8]. Paste A is prepared from 16.2% 20 nm sized TiO_2 and 4.5% ethyl cellulose in terpineol, and Paste B is prepared from 16.2% 200 nm sized TiO_2 and 4.5% ethyl cellulose in terpineol.

The nanoporous TiO_2 electrode was formed on a fluorine doped SnO_2-coated glass substrate (FTO) via screen printing 3 times of Paste A and 1 time of Paste B, respectively. The electrode was then sintered via temperature programming as follows: room temperature raised to 325 °C in 10 min, then maintained for 5 min, 5 min raised to 375 °C and maintained for 5 min, then 5 min raised to 450 °C and maintained for 15 min, 5 min raised to 500 °C and maintained for 20 min in air, and finally cooled to room temperature.

The treatment of metal acetates on TiO_2 surface was performed by the following steps. First the cooled TiO_2 film was dipped in a 70 mmol/L $TiCl_4$ aqueous solution at 70 °C for 30 min and then sintered at above mentioned temperature programming. Then it was dipped in 5 mmol/L aqueous solution of magnesium acetate or manganese acetate for 3 min, followed by washing with de-ionized water and ethanol successively. Finally the modified TiO_2 nanoporous electrodes were sintered at 400 °C for 30 min in air.

For dye sensitization, the modified TiO_2 and bare TiO_2 electrodes were immersed in a 0.5 mmol/L N719 dye solution (tert-butyl alcohol/acetonitrile, v/v = 1) for 24 h at room temperature. For DSSC device fabrication, one drop of electrolyte solution was put on the sensitized TiO_2 electrode which was immediately pressed together with FTO on which a ca. 200 nm thick layer of Pt was thermally evaporated. To ensure stability, the device sides are covered with “SuperGlue®” and epoxy adhesive. The active area of the cells was about 0.25 cm^2 as determined by the cross section of Pt electrode and titanium oxide photoanode.

2.3. Instruments and measurements

X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKα radiation. The base pressure was about 3×10^{-7} Pa. The binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon. X-ray diffraction (XRD) measurements were performed on an X'Pert PRO (PANalytical, Netherlands) with Cu Kα (λ = 0.154056 nm) radiation over the 40 kV voltage and 40 mA current to identify the phase structure of samples. The absorption spectra were recorded on a UV-2550 spectrophotometer (Shimadzu, Japan). The photocurrent-voltage characteristics and electrochemical impedance spectroscopy (EIS) measurements of DSSCs were recorded using an electrochemical workstation (CHI 660C, Shanghai). Simulated AM 1.5 illumination was provided by Xenon lamp solar simulator (Institute of Optoelectronics Technology and Solar Energy Xi'an Jiaotong University). The frequency range was explored from 0.1 Hz to 1 MHz. The applied bias voltage and ac amplitude were set at open-circuit voltage of the DSSCs and 10 mV. The impedance spectra were analyzed by an equivalent circuit model interpreting the characteristics of the DSSCs. The incident photon to current conversion efficiency (IPCE) results were acquired from QE-R3511 (Enli Technology Co. Ltd).

3. Results and discussion

The metal acetate modified TiO_2 electrode surface was characterized by the XPS and XRD. Fig. 1(a) shows the XPS for the magnesium acetate modified TiO_2 electrode. The peak detected at 47.75 eV agrees with the binding energy of 2p electron in Mg indicating the presence of Mg. Peaks at 638.9 and 650.1 eV can be assigned to Mn 2p3/2 and Mn 2p1/2, respectively, which agrees with the binding energies of Mn presence (see Fig. 1(b)). To further confirm the formation of acetate modified TiO_2 electrode, XRD patterns were recorded (see Fig. 2). The peaks at 27.5°and 37.5°correspond to the diffraction of the (300) lattice of cubic MgO (JCPDS file 45-0946) and (−202) planes of Mn(OH)O (JCPDS file 00-041-1379). The peaks at 27.2°and 33.7 are the diffraction from the (110) and (101) planes of TiO_2 rutile powder (JCPDS file 01-073-1765), other peaks are anatase of TiO_2 (JCPDS file 00-021-1272).

Fig. 3(a) shows the J–V curves of DSSCs fabricated from bare and metal acetate modified TiO_2 electrodes under illumination intensity of 100 mW/cm^{-2}. The parameters of DSSC devices were compared in Table 1. The action spectrum of the photocurrent is also shown in the inset of Fig. 3(a). The IPCE reaches a maximum efficiency of 31.6% at 520 nm based on Mg modified DSSC device, which corresponds to the highest energy conversion efficiency of magnesium modified DSSC device. The optical absorption spectra of the dye desorbed from the photoanode surfaces in a 0.1 M NaOH solution can be used to estimate the amount of adsorbed dye molecules. The UV–vis spectra of both

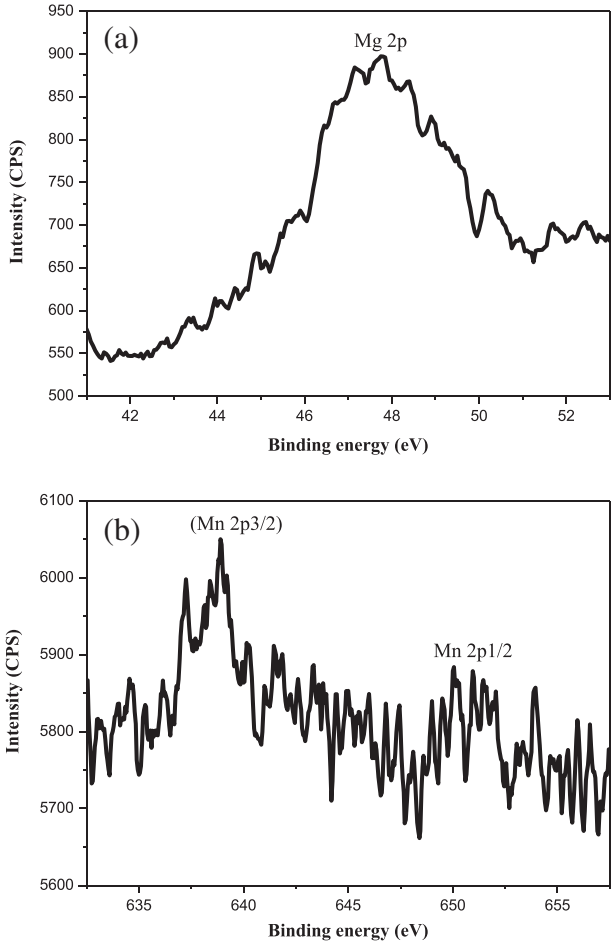

Fig. 1. X-ray photoelectron spectroscopy spectra of (a) Mg 2p, (b) Mn 2p3/2 and Mn 2p1/2 for acetate modified TiO_2 film.