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Letter

Silver-coated TiO_2 electrodes for high performance dye-sensitized solar cells

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ABSTRACT

Silver-coated TiO_2 electrodes were prepared by photodeposition with different light durations. Comparing with the dye-sensitized solar cells (DSSCs) using conventional TiO_2 electrode, the conversion efficiency of DSSCs fabricated with silver-coated TiO_2 electrodes was improved from 5.97% to 6.86%. The Ag layer could reflect incident light and lengthen the optical path in electrodes, and also appropriate Ag particles absorbed on the TiO_2 surface slowed down the electron recombination. The recombination mechanisms of DSSCs were analyzed by open circuit voltage decay (OCVD) measurements, which provide evidence that the charge transfer from the surface state was strongly suppressed by the silver coating.

1. Introduction

Dye-sensitized solar cells (DSSCs) are intensively studied in the last decade due to their low manufacturing cost and potentially high conversion efficiency [1]. In order to improve the performance of DSSCs, some methods such as new sensitizer synthesis, chemical surface modification and design morphology were proposed [2,3]. Among them, decreasing the recombination of electron in the dye or electrolyte and lengthening the optical path within TiO_2 electrode by surface chemical modification may be promising approaches [4]. For example, the conversion efficiency was increased from 5.9% to 6.7% in a ZnO-coated TiO_2 electrode [5]; from 5% to 6% in TiO_2 nanoparticles dressed with gold nanoparticles [6]; from 5.6% to 6.7% in aluminum coating TiO_2 anode [7].

In this study, we explored whether the silver coating by photo-deposition would enhance the solar cell efficiency of the dye-sensitized solar cell, and what precaution should be taken during the employment of this method. By open circuit voltage decay (OCVD) analysis, we tried to reveal the recombination kinetics in Ag-coated electrode in comparison with conventional TiO_2 electrode, and to find out the role of silver in the efficiency improvement [8].

2. Experiment

The DSSCs with an active area of 0.16 cm^2 were assembled as follows. Double-layer photoelectrodes (Fig. 1) consisting of TiO_2 nanoparticles (diameter = 20 nm) as the bottom layer and TiO_2 nanospheres (diameter = 400 nm) as the top layer were fabricated for DSSCs [9,10]. The use of TiO_2 nanospheres remarkably enhanced cell performance due to the light scattering and dye adsorption capabilities. Then the TiO_2 electrodes were soaked in a 5×10^{-4} mol/L $AgNO_3$ solution and the solutions were irradiated by UV light (major wavelength 254 nm, 15 W) for 5, 10, 15 and 30 min separately. Under UV illumination, the electron in valence band were excited to jump to conduction band. Because the Nernstian potential of the conduction band in TiO_2 is lower than the standard electrode potential of Ag^+/Ag, the difference of potential is formed. Thus, the electron will be transferred from conduction band of TiO_2–Ag^+ which was absorbed on the surface of TiO_2 nanospheres, and silver ions are reduced to silver atoms. The X-ray photoelectron spectroscopy (XPS) analysis conducted by Han et al. demonstrated that Ag deposited on the surface of TiO_2 anode was mainly in zero valent and partially in Ag_2O [11].

After drying at room temperature, the Ag-coated TiO_2 electrodes were immersed in a 4×10^{-4} mol/L solution of the dye N719 in dry ethanol for 24 h. The TiO_2 photoelectrodes with N719 were rinsed with anhydrous ethanol and dried again. Also a conventional electrode was fabricated as a control. The counter electrodes were prepared by spin coating a 4 wt% H_2PtCl_6

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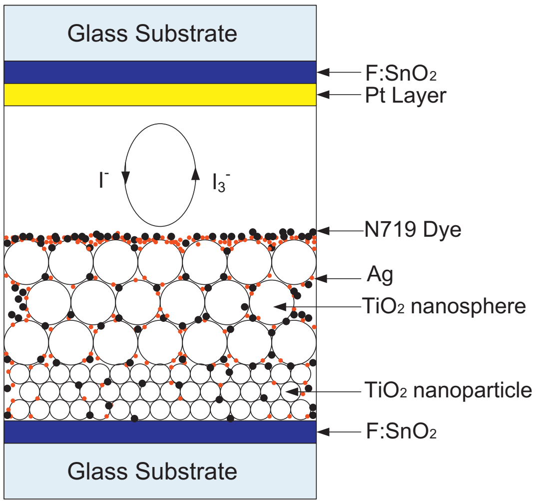

Fig. 1. Schema of the DSSC with an Ag-coated TiO_2 electrode.

isopropanol solution onto the conductive fluorine tin oxide (FTO) glass. All cells were sealed by using a Surlyn polymer film (Du Pont, 25 μm thick), so the space between two electrodes was adjusted to about 25 μm for embarking the liquid electrolyte. A hole in diameter of 1 mm was made on the counter electrode and the cell was heated at 80 °C and 20 Kg pressure for 50 s on a hot plate until the Surlyn film completely melted. The electrolyte was then injected into the spacer between the electrodes by vacuum reverse pressure perfusion. Finally, the hole was completely resealed using a Surlyn film (60 μm thick) and glass [12].

An AM 1.5 solar simulator with a 300 W xenon lamp (San-Ei Pioneer of Light Technology, XES-310S) was used to illuminate the DSSCs, and the incident light power was calibrated to 100 mW/cm^2. The *I–V* curve was obtained using a digital source-meter (Keithley 2400). The incident-photon-to-current conversion efficiency (IPCE) was determined by using Quantum Efficiency Set-up (Newport Instruments). Then OCVD was used to further explore the electron recombination kinetics. In OCVD, the illumination was turned off in a steady state and the subsequent decay of photovoltage (V_{oc}) was monitored. OCVD provides continuous reading of the electron lifetime as a curve of V_{oc} at high-voltage resolution, that contains rich information on the electronic processes of recombination in DSSCs [13,14], as we will show in this paper. A pure white LED light (8 W) and an oscilloscope (Lecroy, Wave Runner 44xi) were used as a light source and a monitoring device respectively for OCVD measurements. The variation of V_{oc} with time after illumination interruption was recorded at an interval of 10^{-4} s. We have omitted the final region of decay at voltages < 50 mV, in which the data were poorly resolved.

Table 1
Performance parameters of DSSCs.

Deposition time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	η (%)	R_s (Ω)
0	12.44	0.720	66.7	5.97	35.37
5	12.98	0.724	68.2	6.46	30.39
10	13.55	0.735	69.4	6.86	28.15
15	12.76	0.730	66.3	6.18	31.53
30	12.22	0.730	57.7	5.15	41.27

3. Results and discussion

Fig. 2 displays the photocurrent–voltage characteristics of the DSSCs separately using Ag-coated and conventional TiO_2 electrodes. Table 1 lists the characteristic values of cell performance. The R_s is series resistance obtained by using one diode equivalent circuit model and Particle Swarm Optimization (PSO) method which we have studied to extract the parameters of the equivalent circuit [15].

The amount of Ag deposited on the porous TiO_2 film had substantial influence on the performance of DSSCs. At a fixed concentration of $AgNO_3$ (5×10^{-4} mol/L) and UV light intensity, the short-circuit photocurrent per unit area (J_{sc}), open-circuit photovoltage (V_{oc}), power conversion fill factor (FF) and efficiency (η) were increased with the deposition time. At the deposition time of 10 min, the J_{sc}, V_{oc}, FF and η all reached the maximum. Compared with the conventional DSSC, J_{sc}, V_{oc}, FF, and η were increased from 12.44 to 13.55 mA/cm^2, 0.72 to 0.735 V, 66.7% to 69.4%, and 5.97% to 6.86% respectively and R_s was decreased from 35.37 to 28.15 Ω.

These results can be attributed to the following facts: (1) J_{sc} increases with the optical path length in TiO_2 electrodes. Thus, the increase of J_{sc} can be explained that at the deposition time of 10 min, enough Ag was deposited on the TiO_2 film, and a thin layer for light reflection was formed on the top of the film. Probably, the thin silver layer reflected part of light and lengthened the light path which will be verified by IPCE. (2) Because of the Ag deposition, electron recombination was slowed down. The suppression of recombination between the electron and the oxidized species

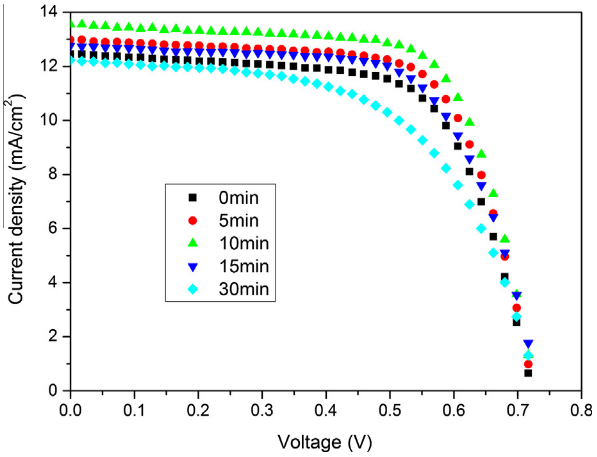

Fig. 2. *I–V* characteristics of conventional DSSCs and TiO_2 electrodes coated with Ag. The treatment time for Ag coating is 5, 10, 15 and 30 min.

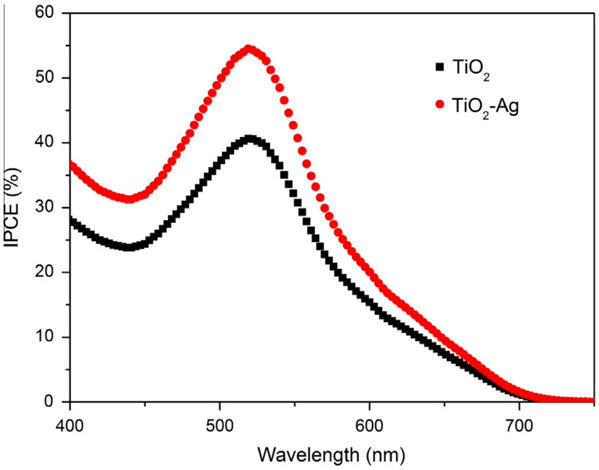

Fig. 3. IPCE spectra of DSSCs using the TiO_2 electrode and Ag-coated TiO_2 electrode at Ag coating time of 10 min.