

Influence of the binder on the electron transport in the dye-sensitized TiO₂ electrode

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Abstract

Surface photovoltage spectroscopy and electric field induced surface photovoltage spectroscopy (EFISPS) were used to study the influence of the polyethylene glycol (PEG) as the binder on the electron transport in the dye-sensitized 7 μm TiO₂ film electrode. The photovoltage of the TiO₂ electrode prepared without PEG was higher than that of the electrode with binder, which showed that the charge transport properties of the TiO₂ electrode were improved in the absence of the binder. After the electrode prepared with the binder was applied with +0.5 V voltage, three photovoltage peaks appeared at 432, 385 and 343 nm in the EFISPS, indicating that there existed impurity states in the electrode due to the carbonization of the PEG. When the TiO₂ electrode prepared with binder was applied to the dye-sensitized solar cell, the photogenerated electrons from the excited dye could be trapped by these impurity states.

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1. Introduction

The Grätzel-type photoelectrochemical cell (DSCs) is considered as a possible alternative to present p–n junction photovoltaic devices and efforts have been devoted to improving its efficiency [1–9]. This kind of cell consists of three components: dye-sensitized TiO₂ photo-electrode, electrolyte, and the counter electrode. The combination of the nanocrystal TiO₂, Ru complex sensitizer and I₃⁻/I⁻ electrolyte has achieved promising conversion efficiency. Nanometer-sized TiO₂ was used because of it being wide-band, stable, cheap, and especially because of its high

surface area, which increased the amount of the dye adsorbed by the electrode [10].

The TiO₂ electrode is the key part of the DSC, which is usually made from colloid TiO₂ by doctor-blade method. In order to avoid the cracking of the TiO₂ electrode, binder, such as polyethylene glycol (PEG), was added to the TiO₂ colloid so that the TiO₂ film became thicker [1]. The preparation method [11], particle size, crystallinity [12], shape of the TiO₂ [13], annealing temperature of the electrode [11], and the adding ratio of the binder [14] affected the transport of the charge in the electrode.

In this paper, we prepared TiO₂ film electrodes with relatively thin thickness (7 μm) with and without binder, which were applied to the dye-sensitized solar cell. The surface photovoltage spectroscopy (SPS) and electric field induced surface photovoltage spectroscopy (EFISPS) revealed the worse transport properties of the photogenerated electrons and the existence of the impurity states

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in the TiO₂ electrodes owing to adding the PEG in the preparation process.

2. Experiment section

2.1. Chemicals

All reagents in our experiments are analytic grade. Sodium hydroxide, iodine, polyethylene glycol (MW=20000), glacial acetic acid, acetonitrile and isopropanol were purchased from Beijing Chemical Co. and used as received. Lithium iodide, titanium isopropoxide, and 3-methyl-2-oxazolidinone (NMO) were purchased from Acros Co. and used as received. TiO₂ (P25) was purchased from Degussa Co. The dye [*cis*-di(isothiocyanato)-bis (4,4'-dicarboxy-2,2'-bipyridine) ruthenium (II)] (N3) was purchased from Solaronix SA Co.

2.2. The preparation of the TiO₂ electrodes

TiO₂ aqueous-sol was prepared according to the reference [15]. 12 ml of deionized water (18 MΩ/cm) was added to the mixture of 20 ml of titanium isopropoxide, 23 ml of glacial acetic acid and 160 ml of isopropanol under vigorous stirring. The theoretic TiO₂ content in the aqueous-sol was 4.3% by weight.

386.4 mg of TiO₂ powder (P25) was added to 2 ml of the above sol, and stirred for overnight, a suspension with 17.5% of the TiO₂ content was obtained. After 187.2 mg of PEG was added to the above suspension and stirred for overnight, we obtained another suspension with 40% PEG of the TiO₂ weight.

A layer of adhesive tape (about 50 μm thick) was stuck to the four edges of the conducting glass (thickness=1 mm, sheet resistance=30 Ω/square). The thickness of the TiO₂ film was controlled by the tape. The suspensions were spread on the conducting glass using a glass rod. After dried in air for 30 min, the electrode obtained from each suspension was

sintered at 450 °C for 30 min. The TiO₂ electrodes prepared with and without binder were then obtained.

2.3. The assembly of the dye-sensitized solar cell

The TiO₂ electrodes with and without binder were immersed in 0.5 mM N3 solution overnight for the sensitization of the TiO₂ electrode. The sensitized electrodes were cohered together with a platinized conducting glass [16] by epoxy resin. The electrolyte consisting of 0.5 M LiI /0.05 M I₂ in 1:1 (v/v) acetonitrile–NMO was admitted to the cells by capillary action.

The desorption of the dye was achieved by dipping the N3-sensitized TiO₂ electrode in the 0.01 M NaOH 1:1 (v/v) ethanol–water solution for 6 h. The amount of dye was determined by measuring the UV–visible absorption spectra [17].

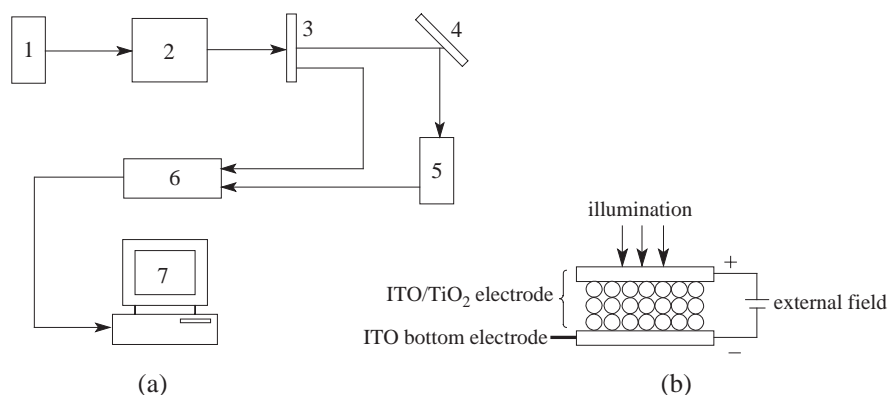
2.4. Instruments

The absorption spectra were measured on the Cary 100 spectrometer (Varian Corp.).

The thickness of the TiO₂ film was confirmed on the Shimadzu SSX-550 scan electron microscope by imaging the profile of the electrode.

X-ray photoelectron spectroscopy (XPS) was carried on the Esca Lab Mark II X-ray Photoelectron Spectrum with Mg Kα X-ray source (1253.6 eV). Charge referencing was determined by setting the C1s from the adventitious carbon contamination at 284.6 eV.

Photocurrent–voltage (*I*–*V*) characteristics were measured with the standard sandwich-type cells. *I*–*V* curves were recorded assisted by an M273 EG&G Princeton Applied Research Scanning Potentiostat/Galvanostat (EG and G Princeton Applied Research, U. S. A). The effective area of the cell was 0.16 cm². A 400-W Xe lamp was used as a light source. Its intensity was about 50 mW/cm² estimated with a radiometer (Photo-electronic Instrument Co. Attached to Beijing Normal University, China).



Scheme 1. Scheme of (a) setup for measurements of SPS and EFISPS and (b) the structure of the photovoltaic cell used in SPS and EFISPS measurement. 1, light source; 2, monochromator; 3, chopper; 4, reflector; 5, photovoltaic cell; 6, lock-in amplifier; 7, computer.

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