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PHOTOCHEMISTRY AND MAGNETOCHEMISTRY

Effect of Formulas of Titanoxide Compositions on the Photovoltaic Characteristics of Solar Cells

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Abstract—The effect the chemical composition of semiconductor titanium compositions (titanium pastes) has on the photovoltaic characteristics of dye-sensitized solar cells is investigated. It is established that the efficiency of solar energy conversion by a photovoltaic cell made with Ti-nanooxide D paste is 5.3%, while that of one made with Degussa P25 paste is 4.7%. These data correlate with the specific surface and sorption ability of semiconductor films.

Keywords: photovoltaics, solar cell, titanium dioxide, dye

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INTRODUCTION

Mesoporous thin semiconductor TiO_2 films are among the main components of dye-sensitized solar cells. To fabricate highly efficient solar cells, titanium oxide films must have large specific surface areas, high light-collecting abilities, a high electron transfer rates, and low charge recombination [1]. In preparing solar cells, TiO_2 films are usually subjected to additional modification because of the insufficient bonding between TiO_2 particles [2]. For example, one way of modifying TiO_2 films is to treat the photoanodes of solar cells with $TiCl_4$ solutions. Such treatment not only forms a blocking layer on the surface of the conducting glass, preventing additional charge recombination in the electrode, but also improves the cohesion of the particles [3, 4]. High efficiency of luminous energy conversion was attained for TiO_2 films prepared hydrothermally in [5]. This is, however, a multistage process that limits its use in serial production. The authors of [6] proposed using pastes based on Degussa P25 with a high degree of particle cohesion by adding anatase TiO_2 with a large specific surface. The results from photovoltaic measurements showed that such modification raises the open-circuit voltage and filling factor of solar cells, and their efficiency of conversion, by 0.3%.

Adding an oxidizing agent to the TiO_2 paste lowers the amount of residual carbon on the TiO_2 surface and improves the adsorption of dye molecules on the surface. The highest efficiency was attained for a cell based on TiO_2 paste with the addition of 2% DNSA [7].

The authors of [8] showed that the composition of pastes greatly affects the microstructure and photoelectrochemical properties of TiO_2 films. In this work, we investigate the effect the chemical composition of titanium pastes has on photovoltaic properties of solar cells sensitized with dye Z907.

EXPERIMENTAL

To prepare our semiconductor films, we used commercially available Ti-nanoxide D paste (Solaronix, Switzerland) and a paste prepared on the basis of Degussa P25 TiO_2: 100 mg of TiO_2 colloid powder was triturated in a porcelain mortar with a small amount of deionized water (2 mL) and acetylacetone (0.2 mL) until a viscous paste formed.

The chemical composition of Degussa P25 paste includes TiO_2 colloid nanoparticles (particle size, 25 nm; anatase form), deionized water, and acetylacetone to prevent the aggregation of TiO_2 nanoparticles. In addition, acetylacetone improves the mechanical stability of the calcined film.

The composition of Ti-nanoxide D includes anatase TiO_2 with nanoparticle sizes of 15–20 nm, water, alcohol, organic solvents, and ethyl cellulose. The organic solvents in the pastes effectively prevent the aggregation of nanoparticles. Polyethylene glycol serves as a binder and a pore-forming component. In addition, these pastes contain ethyl cellulose to regulate the viscosity and rheological properties of pastes, and to promote the formation of a homogeneous TiO_2 film with numerous surface pores.

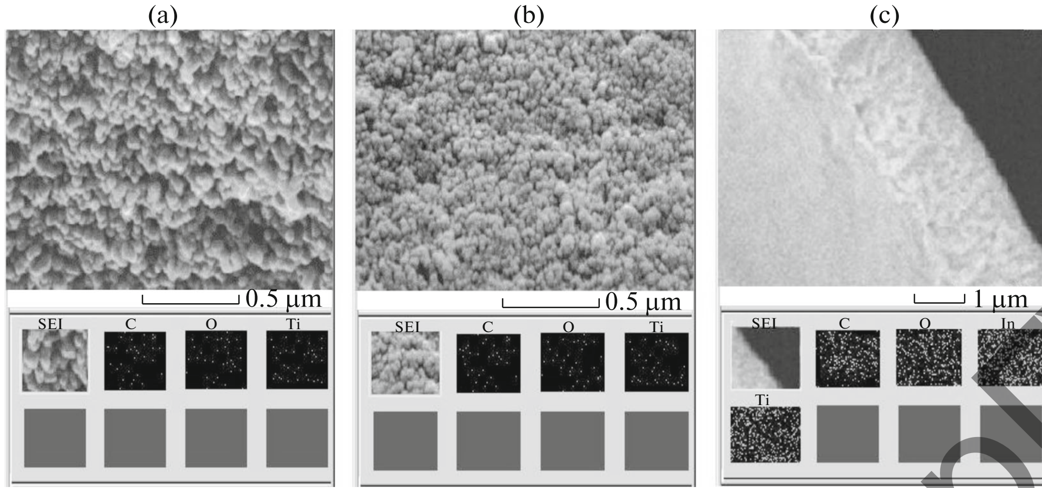

Fig. 1. Microstructures of surfaces of titanium photoelectrodes fabricated using different pastes: (a) Ti-nanoxide D, (b) Degussa P25, and (c) transverse film cut.

To prepare the titanium paste films, we used glass substrates coated with an FTO conducting layer (6 Ω/cm^2, Sigma Aldrich) purified in an ultrasonic bath (PSB-Gals, Russia). After 15 min of ultrasonic treatment, the substrates were washed with distilled water and ethanol. The substrate surfaces were then cleaned by ion etching in argon plasma for 20 min. The paste was deposited on the surface of each conducting glass plate via screen printing. The screen printing procedure was repeated until the appropriate thickness of the semiconductor film was attained. The semiconductor films were then gradually heated in a muffle furnace at 325°C for 5 min, 375°C for 5 min, 450°C for 15 min, and 500°C for 15 min. This procedure resulted in solid films prepared using Degussa P25 and Ti-nanoxide D pastes.

The microstructure of titanium dioxide films prepared using different pastes was investigated using a Tescan MIRA 3MLU electron microscope (Czech Republic). Recorded images of the films' microstructure are presented in Fig. 1.

It can be seen from Fig. 1 that the films' surfaces are granulated and finely grained with an average grain size of 10–25 nm. The film made with Ti-nanoxide D paste has a looser surface, while the one made with the Degussa P25 paste is denser but preserves the porosity of the film surface. Investigation of the films' elemental composition revealed the presence of titanium and oxygen atoms along with negligible amounts of carbon.

The thickness of the titanium photoelectrodes was monitored using the electron microscopy data. Photographs of transverse film cuts were used. The film thickness was 2 μm (Fig. 1).

As sensitizing molecules, we selected the commercially available dye Z907 (*cis*-bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-dinonyl-2'-bipyridyl)ruthenium(II) (Sigma Aldrich), the structural formula of which is presented in Fig. 2. This dye has a high extinction coefficient in the UV and visible regions of the spectrum [4].

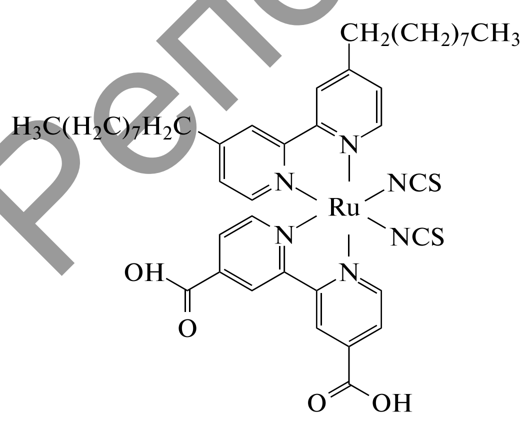

Fig. 2. Structural formula of dye Z907.

Cell surfaces adsorbed dye molecules from ethanol solutions with dye concentrations $C = 10^{-3}$ mol/L. The cells were held in the solutions for 20 h and then extracted and placed in a drying oven at 80°C for 3 h. The number of adsorbed Z907 molecules was determined by the variation in the optical density of the solution before and after sorption.

The specific surfaces of the films were determined using a Sorbi MS measuring complex equipped with an additional SorbiPrep system for preliminary sample treatment (ZAO META, Russia). The specific surface of the film made with Degussa P25 paste was 24.7 m^2/g; for the film made with Ti-nanoxide D paste, $S_{SP} = 119$ m^2/g. The average pore size for 43% of

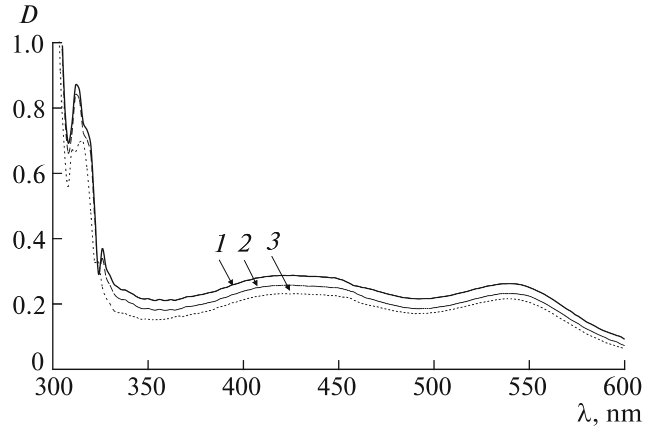

Fig. 3. Absorption spectra of dye Z907 in ethanol (*1*) before and (*2*, *3*) after sorption with porous films based on different pastes. Spectrum *2* corresponds to Degussa P25; spectrum *3*, to Ti-nanoxide D.

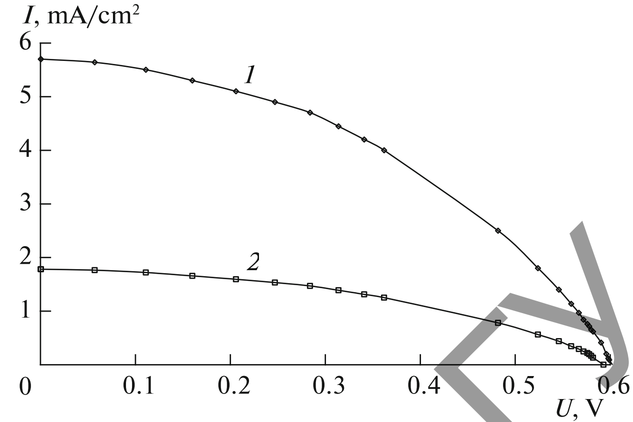

Fig. 4. *I*–*V* characteristics of cells fabricated using different pastes. Characteristic (*1*) corresponds to Ti-nanoxide D; characteristic (*2*), to Degussa P25.

the film made with Degussa P25 paste was 15 nm; for 70% of the film made with Ti-nanoxide D paste, the average pore diameter was 50 nm.

RESULTS AND DISCUSSION

Figure 3 shows the absorption spectra of dye Z907 before and after sorption by cells based on different pastes. It can be seen from Fig. 3 that the cell based on the Ti-nanoxide D paste has the best sorption ability. That of the film made with the Degussa P25 paste is lower. These data correlate with the specific surfaces of the films. The numbers of adsorbed molecules were 0.5×10^{-13} and 0.2×10^{-13} mol/m^2 for the Ti-nanoxide D and Degussa P25 films, respectively.

Earlier, we performed experiments to study the photovoltaic characteristics of cells sensitized with dye Z907. Films of titanium photoelectrodes were prepared according to the standard procedure. Iodolyte Z150 (Solaronix, Switzerland) with an increased concentration of iodide ions was used as the electrolyte for titanium photoelectrodes sensitized with dye molecules. The spacer between the working and extracting electrodes in the solar cells was a Meltonix-grade film 22 μm thick (Solaronix, Switzerland).

The current–voltage (*I*–*V*) characteristics of the solar cells were measured by illuminating the cells with xenon lamp light (luminous power P_{light} = 100 mW/cm^2) using a CT50AAA Cell Tester (Photo Emission Tech., Inc., United States). The open-circuit voltage (U_{oc}) and short-circuit current (I_{sc}) were determined from the measured *I*–*V* characteristics. The filling factor (*FF*) was determined using the formula

$$FF = \frac{(I_{max}U_{max})}{I_{sc}U_{oc}}. \quad (1)$$

The maximum solar cell efficiency was attained at the point of maximum energy, where the current product to the voltage reached the maximum ($P_{el} = I_n U_n$). The current at this point is denoted I_n, while the voltage is denoted U_n. These parameters determine the actual solar cell efficiency. The solar cell efficiency was determined according to the formula

$$\eta, \% = \left(\frac{P_{el}}{P_{light}}\right)100\%. \quad (2)$$

The *I*–*V* characteristics were measured in the photovoltaic mode at room temperature. Figure 4 shows *I*–*V* characteristics of the cells sensitized with dye Z907. The *I*–*V* characteristic is typical of a Gretzel cell. Its operating principle is easily explained: The electrons of the dye molecule are photoexcited when the cell is illuminated with a xenon lamp. Charge carriers are then injected from the dye molecule into the conduction band of the semiconductor. The oxidized dye molecule is reduced by the electrolyte. These processes result in a flow of current in the cell circuit. The current flows until the cell surface is illuminated with light. It should be noted that the system stops generating the current immediately after the cell surfaces cease to be illuminated.

It is seen in Fig. 4 that the voltages for the cells fabricated using different pastes do not differ strongly, but the currents are noticeably different. The cell fabricated using Ti-nanoxide paste D gives higher current than the one fabricated using Degussa P25 paste.

The maximum currents and voltages were 4 mA/cm^2, 0.36 V and 1.3 mA/cm^2, 0.34 V for the cells made with Ti-nanoxide D and Degussa P25 paste, respectively. The short-circuit currents and open-circuit voltages were 5.7 mA/cm^2, 0.6 V and 1.78 mA/cm^2, 0.58 V for the cells made with Ti-nanoxide D and Degussa P25 pastes, respectively. The filling factor of *I*–*V* characteristics was 0.6 and 0.4 for the cells made with Ti-nanoxide D and Degussa P25 pastes, respectively.

The efficiency of the conversion of luminous energy into electrical energy was $\eta = 5.3\%$ for the cell made with Ti-nanoxide D paste; for the cell made with Degussa P25 paste, $\eta = 4.7\%$. It is evident that the cell made with Ti-nanoxide D paste, which has better sorption ability, has a larger area of contact with phosphor molecules. The semiconductor thus acquires more photoelectrons from the dye than the cell made with Degussa P25 paste, for which the specific surface is smaller.

CONCLUSIONS

The effect the chemical composition of titanium pastes has on the photovoltaic properties of solar cells was investigated. It was established that the specific surface of a film made with Degussa P25 paste was 24.7 m^2/g, while that of a film made with Ti-nanoxide D paste was 119 m^2/g. Investigation of *I*–*V* characteristics of the solar cells based on these pastes showed that the efficiency of the conversion of luminous energy into electrical energy by a cell made with Ti-nanoxide D paste was 5.3%. For a cell made with Degussa P25 paste, this efficiency was 4.7%. These data agree with the values of the specific surface and sorption ability of semiconductor films.

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