

# The effect of the DSSC photoanode area based on $\text{TiO}_2/\text{Ag}$ on the conversion efficiency of solar energy into electrical energy

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**Abstract.** A module based on dye-sensitized solar cells with  $\text{Ag}/\text{TiO}_2$  structure was developed. It is shown that the addition of the core-shell structure to the semiconductor film of titanium dioxide, where the nanoparticle  $\text{Ag}$  serves as the core, and the  $\text{TiO}_2$  is shell, increases the coefficient of solar energy conversion into electrical energy. The effect of the photoanode area on the efficiency of conversion of solar energy into electrical energy is studied. It is shown that the density of the photocurrent decreases with increasing of the photoanode area, which leads to a drop in the efficiency of solar cells.

## 1. Introduction

Dye-sensitized solar cells (DSSC) are promising photovoltaic devices using inexpensive materials whose production technology is quite cheap [1, 2]. The disadvantage of DSSC cells is their low efficiency of conversion of solar energy into electrical energy compared to existing photoconverters based on single-crystal silicon. One of the promising methods for increasing the efficiency of conversion of light energy into electrical energy in DSSC cells is the use of surface plasmon resonance, which  $\text{Ag}$  nanoparticles (NP) possess [3]. Due to its high reactivity of silver, direct use of NP  $\text{Ag}$  in DSSC cells is limited due to the possibility of their direct contact with the electrolyte, which will lead to their oxidation. The use of "core-shell" structures, where the nucleus is a metal nanoparticles with plasmon resonance, the shell – a semiconductor metal oxide ( $\text{TiO}_2$ ) will protect the metal NP from oxidation. In addition, the presence of a semiconductor shell will avoid recombination processes between the metal and the dye [4, 5]. Research in this direction is quite active, therefore, it is expected that a large-scale production of organic solar cells using roll-to-roll technology will soon begin. The characteristic area of the photoanode used in the DSSC is  $0.5 \text{ cm}^2$ . With this geometry, the efficiency of one cell is about 11% [6]. In this case, to produce a module of a solar cell with a total area of  $100 \text{ cm}^2$ , dozens of consecutively and in parallel connected such solar cells must be made. Such a technology is not promising, since losses at the contacts between the cells will lead to loss of photocurrent density and lowering of the voltage, and the materials used to connect these cells will lead to an increase in its total cost. Many works are mainly focused on the fabrication of the DSSC module of a cell based on  $\text{TiO}_2$  NP [7], and the manufacturing of a plasmon-enhanced solar cell module is not practical. In addition, the effect of the area of the DSSC photoactive layer on the basis



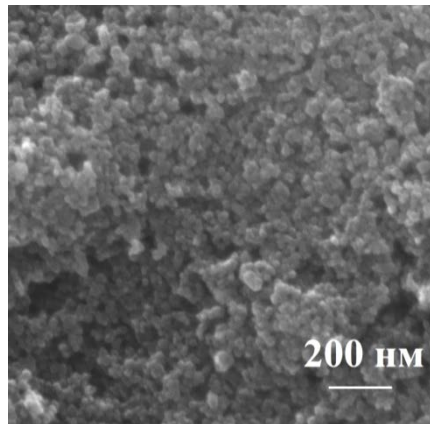
of the Ag/TiO<sub>2</sub> core-shell structure on its efficiency is unknown. In this connection, this work is devoted to the study of the influence of metal NP and the area of the photoactive layer on the efficiency of the solar cell module.

## 2. Experiment

A film of TiO<sub>2</sub> NP was prepared as follows: 50 mg of colloidal TiO<sub>2</sub> (Sigma-Aldrich, >21 nm), triturated in a porcelain mortar with the addition of 2 ml of deionized water and 0.2 ml of acetone. To prevent cracking of the resulting films, polyethylene glycol-sebacate was added to the main paste formulation. The polymer was added to the paste together with ethylene glycol in an amount of 25% by weight with respect to TiO<sub>2</sub>. Stirring was carried out for 48 hours on a magnetic stirrer to form a homogeneous paste. A colloidal solution of silver NP was synthesized by chemical reduction of metal ions from a silver nitrate salt (AgNO<sub>3</sub>) in an ethanol solution. Sodium borohydride (NaBH<sub>4</sub>) was used as the reducing agent. NaBH<sub>4</sub> mass 0.001 g was dissolved in 25 ml of ethyl alcohol. A solution of AgNO<sub>3</sub> in a ratio of 0.0045 g per 10 ml was dissolved in ethyl alcohol. A solution of NaBH<sub>4</sub> cooled to -2 °C was added to the resulting AgNO<sub>3</sub> solution with constant stirring in several stages of 50 µl each. The average particle size of silver was 3.6 nm. To synthesize core-shell structures, the following procedure was used: in 10 ml of the solution of silver NP, 1 ml of a solution of titanium tetraisopropoxide (TIPT (Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>) was added. To synthesize the TiO<sub>2</sub> coating, ethanol solutions of TIPT and silver NP were thorough mixing. The resulting mixture was stirred for 12 hours on a multifunctional rotator PTR-35. The particle size of the core-shell is 25 nm, the particle size of the titanium dioxide is 22 nm. Ag/TiO<sub>2</sub> NP was added during the preparation of the paste. Their concentration in the films was equal to 1 mass% with respect to the mass of the TiO<sub>2</sub> NP. The choice of this concentration of Ag/TiO<sub>2</sub> NP is associated with the optimal concentration of Ag/TiO<sub>2</sub> NP in the manufacture of plasmon-enhanced solar cells sensitized with dye [4, 8]. To obtain porous films based on plasmon core-shell NP and titanium dioxide, the screen printing method was used using the automatic installation Print Screen ATMA AT-45PAB. The films were deposited on FTO substrates (Sigma Aldrich, 8 Ohm/cm<sup>2</sup>). The surface morphology of the films was studied by scanning electron microscopy using the MIRA 3LMU microscope (Tescan, Czech Republic). Geometric dimensions of the deposited films were determined using mesh screens (43 mesh) As a comparison, we obtained films with the area of the photoactive layer: 0.25, 2.25, 4, and 6.25 cm<sup>2</sup>. After drying, the porous films were annealed at the following temperatures and time: 325 °C - 5 min; 375 °C - 5 min; 450 °C - 15 minutes; 500 °C for 15 min. Later the samples were immersed in an ethanol solution of ruthenium dye N719 (Di-tetrabutylammoniumcis-bis (isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II), SigmaAldrich) for 24 hours. Platinum, which was also deposited by screen printing, was used as the counter electrode. Platisol T/SP (Solaronix, Switzerland) was used as a starting material for the production of platinum layer. To form a platinum layer on a conducting electrode, it is necessary to treat it at 500 °C for 1 hour. A 60 µm thick polymer film of Meltonix (Solaronix, Switzerland) serves as a spacer between the working electrode and the platinum electrode in the solar cell. Iodolyte H30 (Solaronix, Switzerland) was used as an electrolyte in a solar cell, which was poured between two glued electrodes through a special hole. Ultrasound soldering station UltrasonicCS55-X151 (CHEERSONIC) was used to obtain the contacts. Solder material is Ecosolder RMA-98. The volt-ampere characteristics of the solar cells were measured by illuminating the cells with the light of a Xe lamp, with a light output of 100 mW/cm<sup>2</sup> (AirMass 1.5) on the CT50AAA measuring complex (PET PHOTO Emission TECH. INC., USA).

## 3. Results

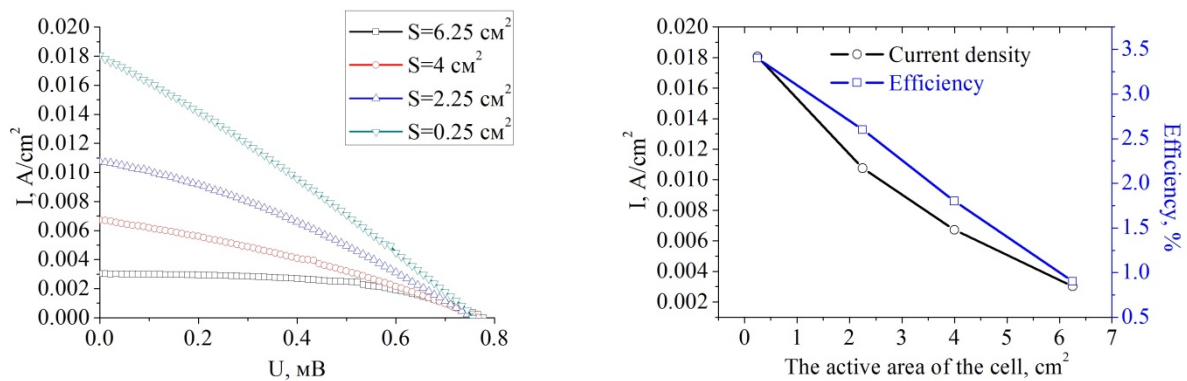
Figure 1 shows a photomicrograph of the surface of the Ag TiO<sub>2</sub> film obtained on a scanning electron microscope.



**Figure 1.** SEM image of a film based on NP Ag/TiO<sub>2</sub>.

It can be seen from the Figure that the surface of the film has a granular structure, there are no visible defects. The use of a screen for the application of films allows the production of films with the same thickness. The study of the transverse cleavage of the sample showed that the film thickness is of the order of 10  $\mu\text{m}$  with a minimum thickness spread of 200 to 500 nm along the entire perimeter.

The influence of the area of the photoactive layer of the solar cell on its efficiency was studied. For this purpose, DSSC was obtained on the basis of the Ag/TiO<sub>2</sub> "core-shell" structure with the area of the photoactive layer of 0.25, 2.25, 4, and 6.25  $\text{cm}^2$ . The results of measurements of the current-voltage characteristics of solar cells are shown in Figure 2.

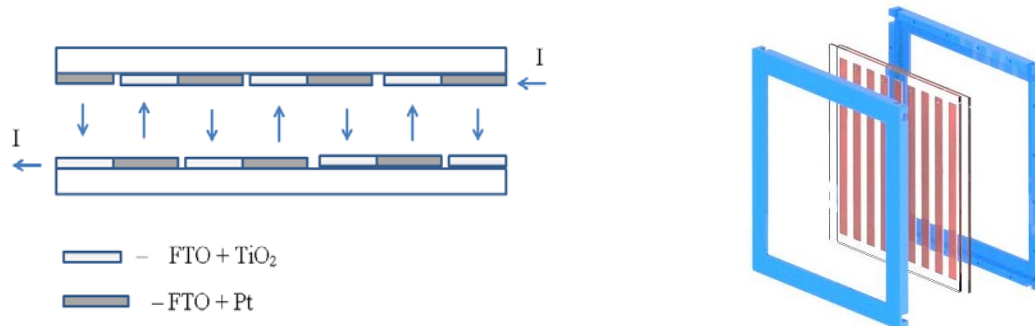


**Figure 2.** I-V characteristics (a) and the effect of the active layer area on the efficiency of a solar cell based on Ag/TiO<sub>2</sub> (b)

From the data presented, it can be seen that the photocurrent density decreases linearly with increasing photoanode area. Thus, for a photoanode area of 0.25  $\text{cm}^2$ , the photocurrent density is equal to 0.018  $\text{A}/\text{cm}^2$ . When the area is increased to 6.25  $\text{cm}^2$ , its value decreases to 0.003  $\text{A}/\text{cm}^2$ . Perhaps this is due to the fact that as the area of the photoactive layer grows, the density of surface defects increases, which are primarily formed as a result of unformed bonds between NPs that form a film. Unformed connections will lead to a sharp increase in recombination processes in the film and will impede the transport of electrons. The reason for the lowering of the current density can also be the low rate of removal of electrons from the surface of titanium dioxide by the platinum counter electrode.

Next, the influence of the Ag/TiO<sub>2</sub> "core-shell" structure composition on the efficiency of the solar cell module was investigated. As it is known, the open circuit voltage of DSSC depends on the position of the quasi Fermi level and the level of the oxidation-vestibular potential of the electrolyte

used. When using the electrolyte Iodolyte H30, the maximum open circuit voltage in the DSSC is about of 0.8 V. But for most electrical appliances, it is necessary to obtain a voltage of the order of 5 V. Therefore, to obtain the required voltage, several cells must be connected in series. With this in mind, we were able to place 9 separate elements connected in series with a total area of 48.6 cm<sup>2</sup> on a FTO conductive glass substrate with the area of 100×100 mm. The geometrical arrangement of the electrodes is shown in Figure 3.



**Figure 3.** Connection scheme for electrodes (the arrow indicates the direction of the electric current) (a) and external view of solar cell module (b).

The modules of solar cells were assembled without and with the addition of Ag/TiO<sub>2</sub> nanoparticles. Under standard conditions, their current-voltage characteristics were measured and their efficiency was determined. The results of the measurement are shown in Table 1.

**Table 1.** IV-characteristics solar modules without and with the addition of NP Ag/TiO<sub>2</sub>.

Sample	$U_{oc}$ , V	$J_{sc}$ , mA/cm <sup>2</sup>	FF	$R_{ser}$ , Ωm	$R_{sh}$ , Ωm	Efficiency, %
Ag/TiO <sub>2</sub>	4.8	0.089	0.06	43	731	1.26
TiO <sub>2</sub>	4.2	0.081	0.06	124	1059	0.93

From the data obtained, it can be seen that the addition of Ag/TiO<sub>2</sub> NP at the concentration of 1% by weight in the semiconductor film of titanium dioxide leads to an increase in the efficiency of the solar cell that results in improving of the basic characteristics of the module. Thus, with the addition of the Ag/TiO<sub>2</sub> "core-shell" structure, the successive  $R_{ser}$  and shunting  $R_{sh}$  resistances decrease.

#### 4. Summary

The effect of the area of the DSSC photoactive layer on the basis of the Ag/TiO<sub>2</sub> "core-shell" structure was investigated. It was found that with an increase in the area of the photoactive film from 0.25 cm<sup>2</sup> to 6.25 cm<sup>2</sup>, the photocurrent density decreases and the cell efficiency decreases. A laboratory module of a solar cell with a total area of 48.6 cm<sup>2</sup> was developed. I-V characteristics were measured and the efficiency of DSSC cells was determined without and with the addition of Ag NP. It is established that the addition of 1 mass% of silver NP to the structure of the titanium dioxide film leads to an increase in the efficiency of the module.

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