Conference Paper

Taking into Account the Increase in the Dye Molecules Absorptivity in Modeling of Graetzel Solar Cell with Metallic Nanoparticles

D.A.KISLOV

Orenburg State University – Russia

Abstract

Using a model developed by Professor Kucherenko M.G. a mathematical description of the effect of metal nanoparticles on the absorbing capacity of organic dye molecules in Graetzel cells was carried out. The enhanced absorption spectra of the dye-nanoparticle system and the current-voltage characteristics of the investigated solar cells are calculated.

Corresponding Author:
D.A.KISLOV
r-fizik@yandex.ru

Received: 28 January 2018
Accepted: 15 March 2018
Published: 25 April 2018

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the PhIO Conference Committee.

1. INTRODUCTION

One way to increase the efficiency of the dye-sensitized solar cells is to add metal nanoparticles to the titanium dioxide porous layer.

At present, a number of experimental studies have been published [1-4] in which the effect of metal nanoparticles on the work of cells, in particular on the efficiency, is shown. A unique feature of metallic nanoparticles is the generation of very strong local electric fields (the so-called near field or field in the near zone) when light quanta of a certain frequency are absorbed (plasmon resonance).

In the Graetzel cells, the key element of the construction is the dye molecules. They absorb photons and inject photoelectrons into the conduction band of titanium dioxide. The various optical characteristics [5-8], in particular the absorption cross section, vary to a great extent in the dye molecule entering the zone of the amplified electric field.

In our opinion, a change in the absorption cross section of dye molecules by metal nanoparticles is a key effect in the modeling of plasmon solar cells of Graetzel. The basic idea of increasing the dye-sensitized solar cells efficiency is shown in Figure 1.

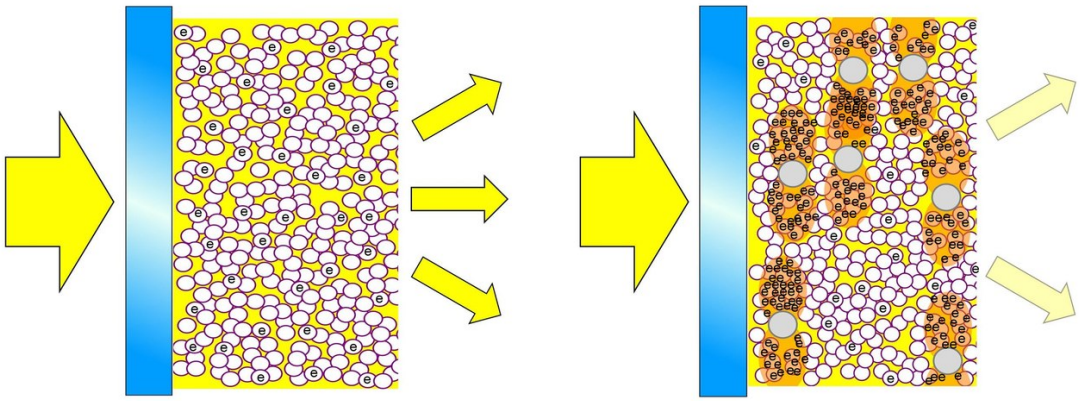

Figure 1: Dye molecules in the Graetzel cell, trapped in the region of the locally enhanced near-field of a metallic nanoparticle, generate more free charge carriers [1].

2. MATHEMATICAL MODEL OF A DYE-SENSITIZED SOLAR CELL BASED ON THE DIFFUSION EQUATION

The work of Graetzel cells in stationary and nonstationary regimes can be described using the diffusion equation with the generation and recombination terms:

$$G(x) + D_e \frac{\partial^2 n(x,t)}{\partial x^2} - R_e(x,t) = \frac{\partial n(x,t)}{\partial t}, \tag{1}$$

with initial and boundary conditions:

open circuit mode	short circuit mode	work mode
$\begin{cases} n(x,0) = n_{eq} \\ \frac{\partial n(0,t)}{\partial x} = 0 \\ \frac{\partial n(d,t)}{\partial x} = 0 \end{cases}$	$\begin{cases} n(x,0) = n_{eq} \\ n(0,t) = n_{eq} \\ \frac{\partial n(d,t)}{\partial x} = 0 \end{cases}$	$\begin{cases} n(x,0) = n_{eq} \\ \frac{\partial n(0,t)}{\partial x} = -\frac{j}{qD_e} \\ \frac{\partial n(d,t)}{\partial x} = 0 \end{cases}$

where, $n(x,t)$ - photoelectron concentration; n_{eq}– equilibrium electron density without illumination; j - current density; q - elementary charge; D_e - diffusion coefficient; d – thickness of the titanium dioxide porous layer (in calculations it was equal to 40 microns).

The speed of photoelectrons generation in equation (1) is determined by the Bouguer-Lambert-Beer law:

$$G(x) = \eta_{inj} \int_{\lambda_{\min}}^{\lambda_{\max}} \alpha(\lambda) I_0 Exp\left[-\alpha(\lambda)x\right] d\lambda \tag{2}$$

where, $\eta_{inj} = 0,9$-the coefficient of electron injection from excited dye molecules into the conduction band TiO_2; $\alpha(\lambda)$– the absorption coefficient of a dye sensitized film of titanium dioxide; I_0– intensity of incident light.

The rate of recombination of photoelectrons in a Graetzel solar cell can be described by expression (3):

$$R_e(x,t) = \frac{n(x,t) - n_{eq}}{\tau_e}, \tag{3}$$

where $\tau_e = 23\,ms$– lifetime of the injected electron.

The values of the parameters for modeling are taken from the works [9-12].

3. EFFECT OF SILVER NANOPARTICLES ON THE ABSORPTION CAPACITY OF ORGANIC DYE MOLECULES

For a mathematical description of the metal nanoparticles effect on the organic dye molecules absorbing capacity, a model developed by Professor M.G. Kucherenko was used [13].

The change in the rate of photons absorption by the dye molecule is associated with an additional dipole moment, which arises on the dye molecule due to the electromagnetic field reflected by the nanoparticle.

The expression for the probability of an electronic transition in a dye molecule with a dipole moment p in the presence of a metal nanoparticle is written as follows [14]:

$$w(\omega, r, \theta, \xi, \varphi - \psi) = \left(\frac{pE_0}{\hbar}\right)^2 \frac{\gamma_D}{(\omega - \omega_{if})^2 + \gamma_D^2} \times$$
$$\times \left(\cos^2\xi + \frac{Re\beta(\omega)}{r^3}\left\{\cos^2\xi + 3\cos^2\xi\cos 2\theta + \frac{3}{2}\sin 2\xi \sin 2\theta \cos(\varphi - \psi)\right\} + \right. \tag{4}$$
$$\left. + \frac{|\beta(\omega)|^2}{4r^6}\left\{\cos\xi + 3\cos\xi\cos 2\theta + 3\sin\xi\sin 2\theta\cos(\varphi - \psi)\right\}^2\right)$$

where $\beta(\omega)$ - polarizability of a metal nanoparticle, E_0 - the electric field.

The transition probability depends on the coordinate r, the angles $\theta, \xi, \varphi - \psi$ (which determine the direction in the space of the transition dipole moment of the dye molecule), the frequency of the electromagnetic field ω, the characteristics of the photochromic molecule (ω_{if} - is the resonant frequency of the transition between the ground and excited states of the molecule, and γ_D– the width of the absorption band of the dye). It is obvious that the first term in (4) corresponds to the case of a dye absorption without nanoparticles.

It should be noted that the dependence (4) is characteristic for one pair of "nanoparticle-dye". For a macroscopic system, for example, for a dyed porous layer of titanium dioxide with metallic nanoparticles, it is necessary to average over the angles and the radial coordinate.

However, a complete account of all the microparameters of the solar cell model with metal nanoparticles is extremely complicated in view of the very complex geometry of the system (Fig. 2). To simplify further calculations, we shall perform an angular and spatial averaging of the transition probability in the approximation of the homogeneous and isotropic distribution of dye molecules with respect to silver nanoparticles.

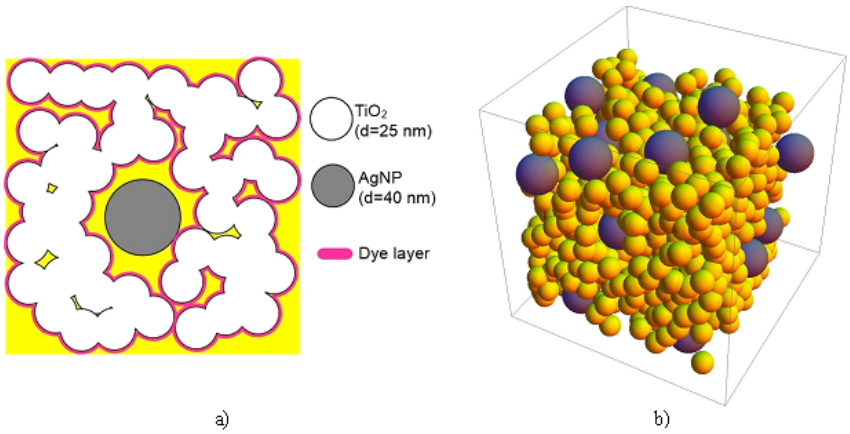

Figure 2: The two-dimensional scheme (a) and the three-dimensional model (b) of the Graetzel solar cell with silver nanoparticle.

The concentration of metal nanoparticles in a porous layer of titanium dioxide can be related to the average distance between nanoparticles $d \sim 1\Big/\sqrt[3]{n_{NP}}$. Then the expression for the transition probability, taking into account the averaging over the radial and angular coordinates of the dye molecules distribution, is written as follows [14]:

$$W(\omega) = \frac{1}{V}\int_{R_{NP}}^{d2}\left(\frac{pE_0}{\hbar}\right)^2 \frac{\gamma_D}{(\omega-\omega_{if})^2+\gamma_D^2}\left(1+\frac{8Re\beta(\omega)}{\pi^2 r^3}+\frac{(7\pi^2+8)\,|\beta(\omega)|^2}{5\pi^2 r^6}\right)4\pi r^2 dr, \tag{5}$$

where, V– volume of integration, R_{NP} – radius of a metal nanoparticle.

Further calculations were used three concentrations of metal nanoparticles: $1.87\times 10^{14}cm^{-3}$, $1.03\times 10^{15}cm^{-3}$,$1.87\times 10^{15}cm^{-3}$.

4. RESULTS OF CALCULATIONS

4.1. Increase in the absorptivity of dye molecules using metal nanoparticles

In the calculations, two types of nanoparticles were used: gold and silver. Experimentally measured complex refractive indices were used to simulate their plasmon properties [15].

Figure 3 shows the normalized absorption spectra of anthocyanin-dyed titanium dioxide porous electrodes with the addition of metal nanoparticles. On the graphs there are two expressed maxima: the first arises from the absorption of photons by dyed titanium dioxide, and the second is due to absorption by the metal nanoparticles (for the samples with gold nanoparticles the maxima practically coincide).

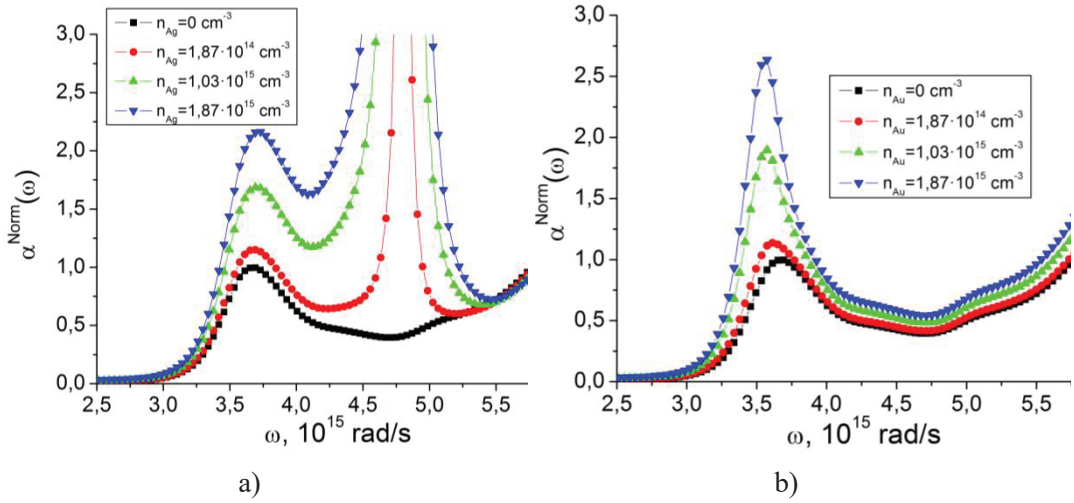

Figure 3: An increase in the absorptivity of anthocyanin molecules in the presence of metal nanoparticles of different concentrations: a) silver; b) gold.

Note that the absorption capacity at the maximum of the anthocyanin absorption band (509 nm) is increases more than 2 times when added to the porous structure of metal particles with concentration $1.87 \times 10^{15} cm^{-3}$. As noted above, this is due to the additional dipole moment induced by the nanoparticle of the metal on the dye molecule.

4.2. Effect of metal nanoparticles on the photoelectrons generation

Plasmon amplification of the dye molecules absorption results in the injection of more photoelectrons into the conduction band of TiO_2. Figure 4 shows graphs of the dependence of the generation term on the coordinate.

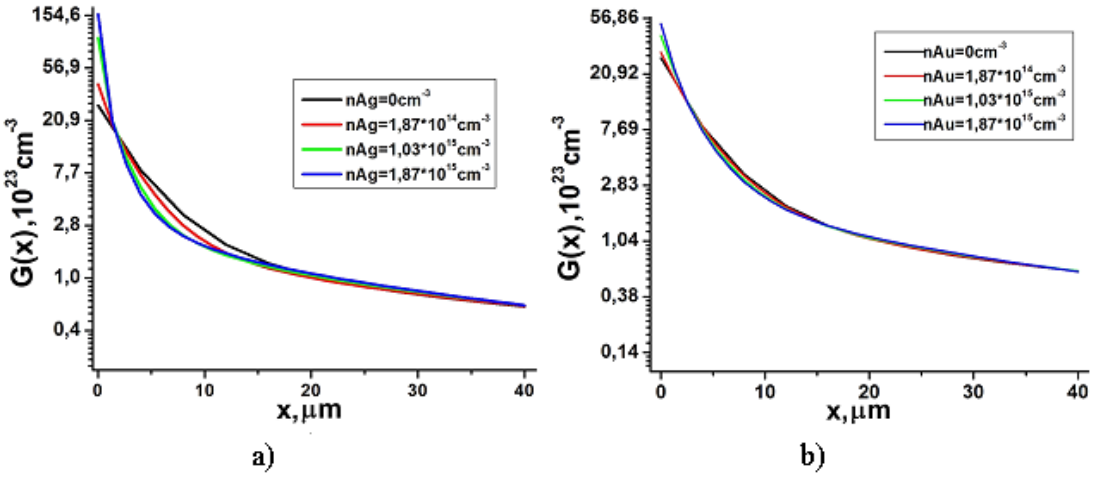

Figure 4: Distribution of photoelectrons injected into the conduction band of porous titanium dioxide at different concentrations of metal nanoparticles: a) silver; b) gold.

Due to the fact that the absorbing capacity of dye molecules increases with the addition of metal to the structure of nanoparticles, more photoelectrons are generated in the near-surface regions of the anode layer. This leads to the fact that at high concentrations of metallic nanoparticles, light penetrates less into the depth of the sample. In addition, it is worth noting that, due to a better combination of the spectral properties of anthocyanin and silver nanoparticles, the latter have a stronger effect on the generation of photoelectrons.

4.3. Effect of plasmon nanoparticles on the stationary mode of operation of Graetzel cells

Figures 5 and 6 shows the calculated data on the spatial distribution of photoelectrons in the anode without and with the addition of noble metal nanoparticles in the stationary mode of operation of the solar cell. Calculations have been made for the cases when the cells operate in the short-circuit mode (Figure 5) and in the idle mode (Fig. 6). It should be noted that, as in the previous calculations, silver nanoparticles exert a greater influence on the work of solar cells of Graetzel than gold ones.

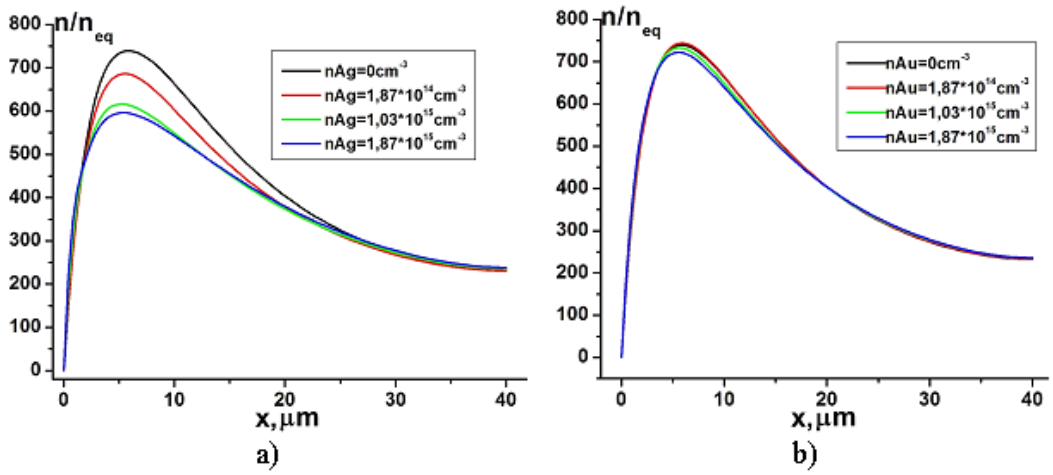

Figure 5: Spatial distribution of photoelectrons in the anode layer at different concentrations of metal nanoparticles: a) silver; b) gold. Short circuit mode.

On the graphs of the spatial distribution of photoelectrons in the anode layer in the short-circuit mode (Fig. 5), despite the fact that the amplitude of the curve decreases with increasing concentration of metal nanoparticles, the gradient of the photoelectron concentration in the near-surface region increases. This results in the cell generating a larger short-circuit current.

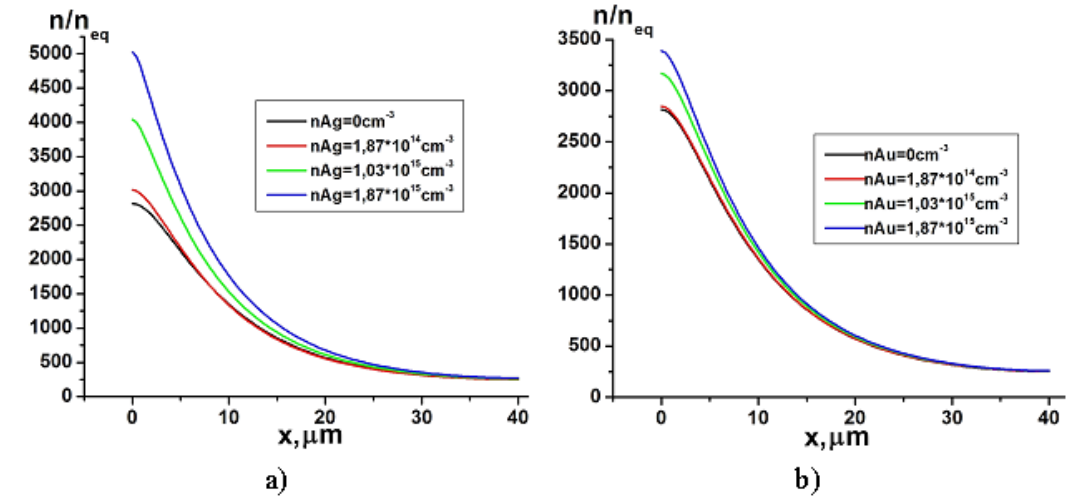

Figure 6: Spatial distribution of photoelectrons in the anode layer at different concentrations of metal nanoparticles: a) silver; b) gold. Open circuit mode.

As noted above, this effect is associated with an increase in the absorption of photons in the near-surface regions of the anode layer due to plasmon nanoparticles.

When considering the spatial distribution of photoelectrons in the anode layer in open circuit mode (Fig. 6), one should note a monotonous increase in the concentration of injected photoelectrons with an increase in the number of plasmon nanoparticles in the sample under study. Calculations show that for the used concentrations of silver

nanoparticles, an increase of 2 times the concentration of photoelectrons in the surface region of the anode porous layer of titanium dioxide (Figure 6a). For samples with gold nanoparticles, the concentration of photoelectrons increases to 1.3 times (Fig. 6b). The increase in the concentration of photoelectrons in the anode layer obtained during calculations as a result of interaction with plasmon nanoparticles should be reflected in an increase in the value of the open circuit voltage of the cell samples under study.

Using the obtained data on the effect of plasmon nanoparticles on the absorptivity of dye molecules, the current-voltage characteristics of the Graetzel cells shown in Fig. 7 were calculated. It can be seen that as the concentration of silver nanoparticles increases in the structure of the solar cell, the short-circuit current density increases from 1.33 mA/cm^2 to 2.33 mA/cm^2, and for samples with gold particles, the current density increases from 1.33 mA/cm^2 to 1.55 mA/cm^2. In both cases, the open circuit voltage is slightly increased.

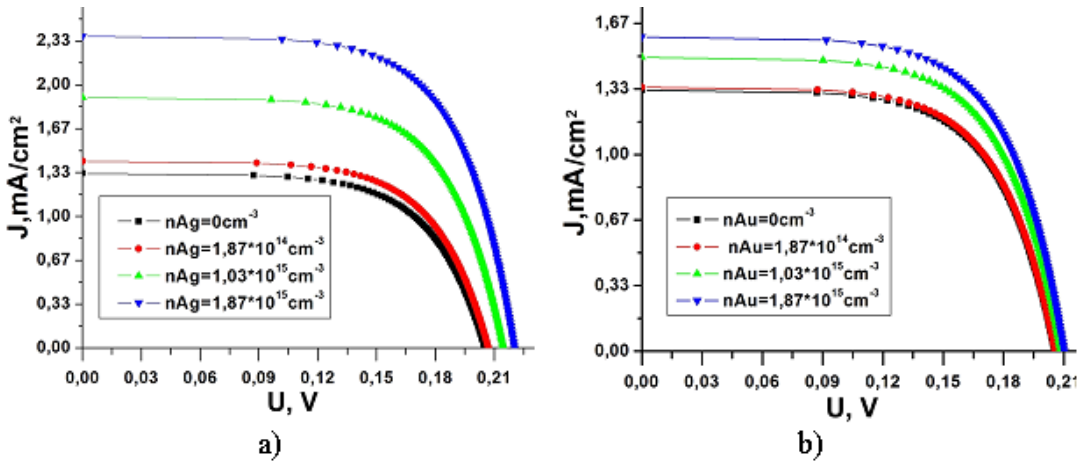

Figure 7: Calculated current-voltage characteristics of the Gretzel cells for different concentrations of metal nanoparticles: a) silver; b) gold.

For a more detailed analysis of the effect of plasmon nanoparticles on the stationary mode of operation of Gratzel cells, the dependences of the relative efficiency and filling factor on the concentration of metal nanoparticles in the anode layer of solar cells were calculated. The graphs are shown in Figures 8 and 9 respectively. Calculations give an increase in efficiency to 20% in the case of using gold nanoparticles and an increase of 2 times for silver nanoparticles.

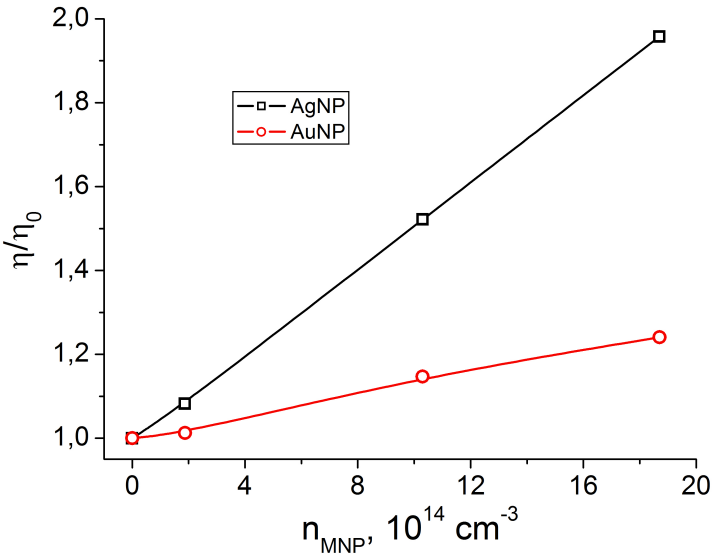

Figure 8: Dependence of relative efficiency on the concentration of plasmon nanoparticles.

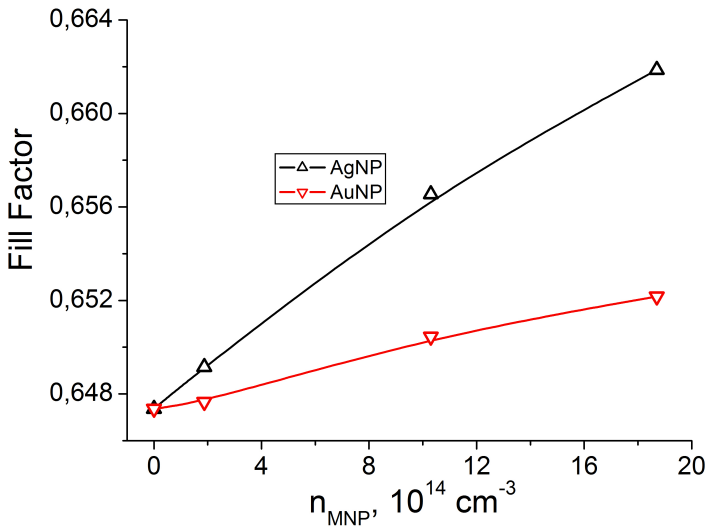

Figure 9: Dependence of the filling factor on the concentration of metal nanoparticles.

5. COMPARISON OF SIMULATION RESULTS WITH EXPERIMENT

Figure 10 shows the experimentally measured current-voltage characteristics of the Graetzel cells and the relative efficiency with the addition of different amounts of silver nanoparticles to the design. The graphs are taken from [1].

Comparison of the obtained results with the results presented in Fig. 10 and in [2-4] gives a good qualitative and quantitative agreement.

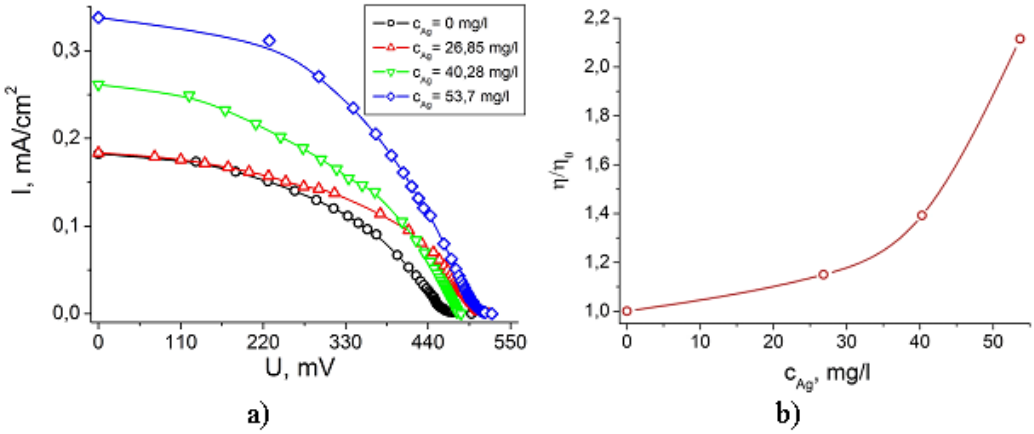

Figure 10: Results of the experiment [1]: a) the current-voltage characteristic of the Graetzel cells with the addition of different concentrations of silver nanoparticles to the structure; b) the dependence of the relative efficiency of cells on the concentration of silver nanoparticles.

As a result of the research it was shown that one of the mechanisms of the plasmon nanoparticles effect on the photocells operation parameters is the plasmon amplification of the dye molecules absorptive capacity.

Acknowledgements

The author acknowledge the support of the Russian Foundation for Basic Research (15-08-04132/17_a) and Council President of the Russian Federation on grants for state support of young Russian scientists (SP-1340.2015.1).

References

[1] Kislov D.A. // Physics Procedia, 2015, **73,** 114

[2] Siu-Pang Ng, et al. // Solar Energy, 2014, **99**, 115

[3] Qi J., et al. // ACS Nano, 2011, **5**(9), 7108

[4] Wooh S., et al. // J. Mater. Chem. A, 2013, **1**, 12627

[5] Craighead H.G., et al. // Opt. Lett., 1981, **6**(5), 248

[6] Kucherenko M.G., et al. // Journal of Applied Spectroscopy, 2014, **81** (3), 416

[7] Kucherenko, M.G., Nalbandyan, V.M. // Russian Physics Journal, 2017,**59** (9), 1425

[8] Kucherenko M.G., Kislov, D.A. // JPPA: Chem., 2017, (in press) DOI: 10.1016/j.jphotochem.2017.10.020

[9] Tayyan A. // Journal of Electron Devices, 2011, **11**, 616

[10] Bavarian M., et al. // Industrial & Engineering Chemistry Research, 2014, **53**, 5234

[11] Filipic M., et al. // Current Applied Physics, 2012, 12, 238
[12] Andrade L., et al. // Solar Energy, 2011, **85**, 781
[13] Zeynidenov A.K., Ibraev N.H., Kucherenko M.G. // Vestnik OSU, 2014, **9**(170), 96
[14] Rusinov A.P., Kucherenko M.G. // Vestnik OSU, 2015, **15**(188), 195
[15] Johnson P. B., Christy R. W.// Phys. Rev. B., 1972, **6**, 4370