



# Plasmonic Effect of Ag Nanoparticles on Polymethine Dyes Sensitized Titanium Dioxide

Niyazbek Ibrayev,<sup>1,\*</sup> Gulden Omarova,<sup>1</sup> Evgeniya Seliverstova,<sup>1</sup> Alexander Ishchenko<sup>2</sup> and Nurxat Nuraje<sup>3,\*</sup>

## Abstract

The effect of core@shell nanostructure of Ag@TiO<sub>2</sub> on the spectral-luminescence properties of polymethine dye (PD) functionalized with sulfonate group and its photovoltaic properties in the PD dye-sensitized solar cell were investigated. Quenching in the fluorescence intensity of PDs molecule by almost 3 times was observed for the dye-absorbed titanium dioxide porous film. Furthermore, the decreasing effect in fluorescence lifetime was found to be significant for the PD molecules modified with functional groups. In the presence of Ag@TiO<sub>2</sub> nanoparticles (NPs), an increase in the luminescence intensity of PD by 60 – 90 % was observed. A mechanism of plasmon nanoparticles' effect on the decay of the excited states of dye molecules was proposed. The efficiency of PD-sensitized solar cells was increased by 1.2 times for PD 1 and 2.0 times for PD 2. The enhancement in the efficiency is result from the growth in the spectral sensitivity of solar cell in the region of 400 – 450 and 600 – 700 nm and a change in the charge-transport parameters of TiO<sub>2</sub> films. This increase was supported by a decrease in the resistance at the semiconductor–dye interface by 8.2 times for PD 1 and 22.4 times for PD 2 that leads to the growth in the part of photoelectrons reaching the counter electrode in solar cell with plasmon NPs.

**Keywords:** Dye-sensitized solar cell; Polymethine dye; Plasmon; Core-shell structure; Optical properties.

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## 1. Introduction

Dye-sensitized solar cell (DSSC) has been developed more than 20 years ago and still interest of specialists.<sup>[1]</sup> Its popularity is ascribed to low production cost, stability, transparency and flexibility compared to other photovoltaic units.

In the DSSC, the function of metal complex dyes, adsorbed on the semiconductor layer, is to harness solar energy. For example, Ru-polypyridine dyes are the major dyes used in the Grätzel cell since they possess high absorption characteristics and chemical stability. The efficiency of DSSCs varies in the range of 7 – 12 % in terms of the dyes applied.<sup>[1b, 1c]</sup> Porphyrin complexes are also

actively used and their maximum efficiency of cells can reach 13%, while DSSCs consisted of them demonstrate an efficiency of about 3 – 5%.<sup>[2]</sup>

Despite all the advantages of metal complexes, their synthesis is a very time-consuming and expensive. Metal-free organic donor-acceptor dyes can be prepared with relatively low costs and well-established synthesis methods. The main advantage of dyes without metal ions is their tunable absorption and electrochemical properties, which can be achieved with an appropriate dye synthesis strategy.

Today, progress in the utilization of non-metallic dyes for the DSSC has been observed. For instance, Ref.<sup>[3]</sup> reported 14.3% of solar cell efficiency for the DSSC co-sensitized with two functionalized carbazole oligothiophenes. As a result of using of two dyes, the spectral sensitivity of the DSSC in the visible region of the spectrum was increased. The authors of Ref.<sup>[4]</sup> have achieved a cell efficiency of 17.3% as chlorine-substituted graphdiyne applied in organic solar cells. A similar approach was also implemented in Refs.,<sup>[5]</sup> where the Förster resonance energy transfer was used to improve light harvesting, as well as to increase the efficiency of photogeneration of charge carriers.

Metal-free dyes are a good alternative to metal complexes, because they are cheap and easy to be synthesized or to be

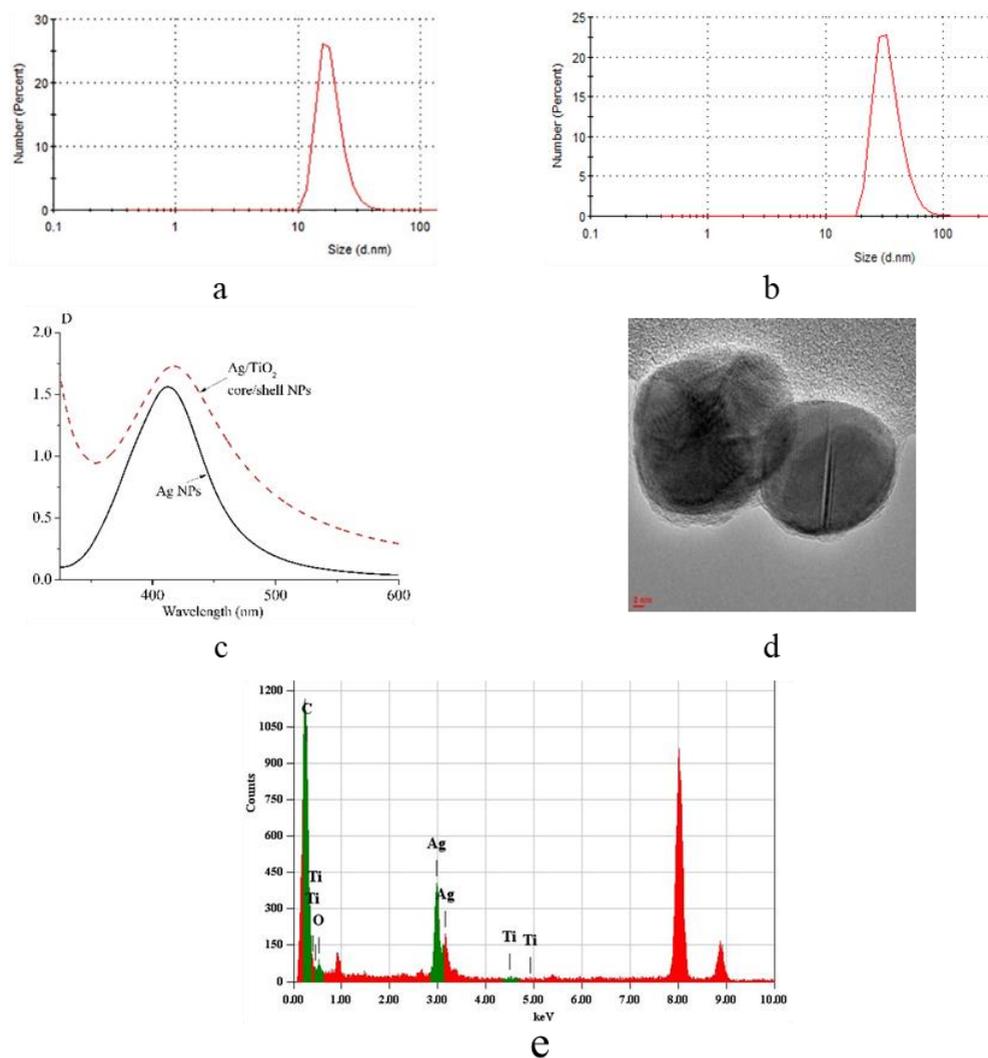
<sup>1</sup> Institute of Molecular Nanophotonics, Buketov Karaganda University, 100028 Karaganda, Kazakhstan.

<sup>2</sup> Institute of Organic Chemistry, NAS of Ukraine, 02660 Kyiv, Ukraine.

<sup>3</sup> Department of Chemical & Materials Engineering, School of Engineering and Digital Sciences, Nazarbayev University, 010000 Nur-Sultan, Kazakhstan.

\*Email: [niyazbrayev@mail.ru](mailto:niyazbrayev@mail.ru) (N. Ibrayev), [nurxat.nuraje@nu.edu.kz](mailto:nurxat.nuraje@nu.edu.kz) (N. Nuraje)





**Fig. 1** Size distribution (a, b), absorption spectra (c), TEM image (d) and EDA analysis (e) of Ag NPs before (a, c) and after (b-e) synthesis of TiO<sub>2</sub> shell.

The Cell Tester Model # CT50AAA (Photo Emission Tech., Inc., United States) was used to measure the photovoltaic parameters of prepared solar cells with plasmon nanostructures. The samples were illuminated with the 1.5 AM Xe lamp. From the obtained data of the open circuit voltage, short circuit current, the fill factor, the value of the efficiency of the cells was determined.

The efficiency of TiO<sub>2</sub> film sensitized by PDs in the presence of core@shell NPs was studied from the curves of dependence of efficiency of solar cells via wavelength of irradiation. The necessary wavelengths region was divided with the using of optical cut-off filters placed after Xe lamp. The intensity of light for each wavelength region was normalized for maximum transmittance.

Z – 500PRO impedance meter (Elins) was used to study the kinetics of transport and recombination of charge carriers for the samples under illumination of a Xe lamp. Data analysis was performed using the EIS-analyzer software, while the electric transport properties of the films were calculated according to the methodology of works<sup>[16]</sup>:  $\tau_{eff}$  –

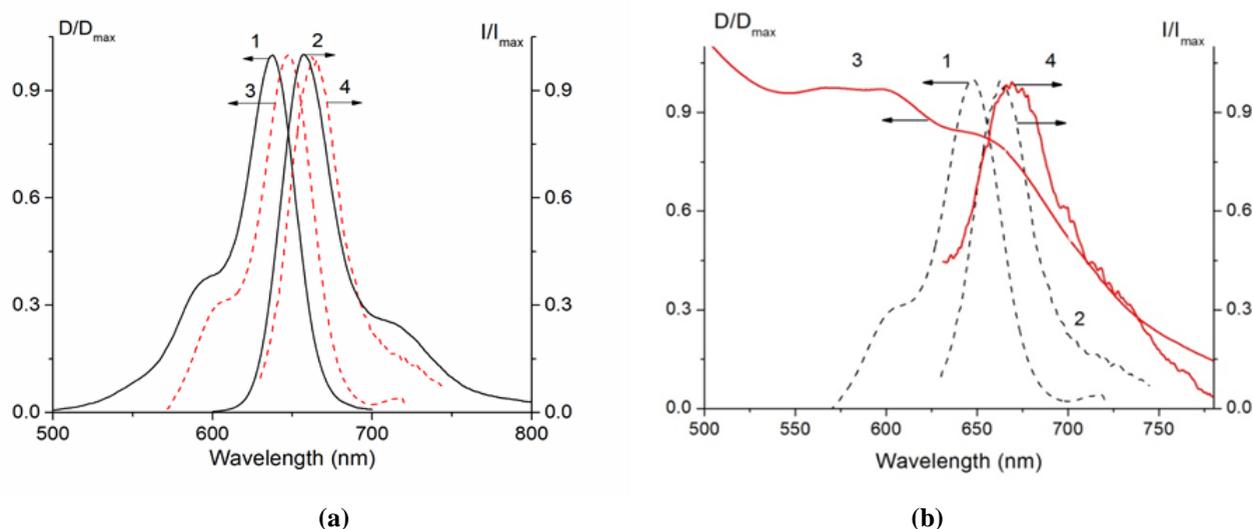
effective electron lifetime,  $R_w$  – electron transport resistance in a titanium dioxide film,  $R_k$  – charge transfer resistance ( $R_k = R_{w\ max} - R_{w\ min}$ ), associated with electron recombination.

### 3. Results and its discussions

In order to elucidate the effect of functional groups on the spectral and luminescent characteristics of PDs, their absorption and fluorescence spectra were measured in ethanol solutions (Fig. 2a).

As the measurements showed, the absorption bands of PD 1 and 2 are located in almost the same spectral range and have a similar shape with a vibrational maximum at the short-wavelength edge.<sup>[6a]</sup> This is a consequence of the fact that they have almost the same chromophore.

The short-wavelength maximum ( $\lambda_{2\ max}$ ) is at 600 – 605 nm exhibits as a shoulder on the dye absorption curve. The half-width of the spectra  $\Delta\lambda_{1/2}$  and the extinction coefficients  $\epsilon$  of the studied PDs are close in value.



**Fig. 2** (a) Normalized absorption (1, 3) and fluorescence spectra (2, 4) of dyes: 1 – 1, 2; 2 – 3, 4. (b) Normalized absorption (1, 3) and fluorescence (2, 4) spectra of dye 2 in ethanol (1, 2) and TiO<sub>2</sub> (3, 4).

**Table 1** Spectral parameters\* of PDs in solutions at C=10<sup>-4</sup> mol/L.

Dye	<sup>a</sup> λ <sub>1 max</sub> , nm	<sup>a</sup> λ <sub>2 max</sub> , nm	Δλ <sup>a</sup> <sub>1/2</sub> , nm	ε·10 <sup>5</sup> , L/mol cm	<sup>f</sup> λ <sub>1 max</sub> , nm	<sup>f</sup> λ <sub>2 max</sub> , nm	Δλ <sup>f</sup> <sub>1/2</sub> , nm
PD 1	640	600	45	2.13	655	715	31
PD 2	646	605	46	2.30	663	730	32

\* <sup>a</sup>λ<sub>1 max</sub> – maximum of absorption spectra, <sup>a</sup>λ<sub>2 max</sub> – maximum of shoulder in absorption spectra, <sup>f</sup>λ<sub>1 max</sub> – maximum of fluorescence spectra, <sup>f</sup>λ<sub>2 max</sub> – maximum of shoulder in fluorescence spectra, Δλ<sub>1/2</sub> – half-width of absorption or fluorescence spectra, ε – extinction coefficients.

On the porous surface of TiO<sub>2</sub> films, a bathochromic shift of the absorption and fluorescence spectra of the studied PDs was observed (Table 2). The shift of the absorption spectrum is greater for functionalized dyes and the intensity of the short-wavelength maximum of the absorption spectra of dyes onto the TiO<sub>2</sub> surface is increased significantly (Fig. 2b).

The fluorescence spectra of dyes in the adsorbed film are also bathochromically shifted relative to the emission bands of PDs in solution. In this case, the fluorescence lifetime (τ<sub>fl</sub>) of the dyes is decreased, which indicates that photoinduced

electron transfer is carried out upon irradiation of PDs on the TiO<sub>2</sub> surface.<sup>[17]</sup>

It should be noted that for the PD 2 dye with sulfonate groups, τ<sub>fl</sub> on the surface of the TiO<sub>2</sub> film was decreased 3 times in comparison with τ<sub>fl</sub> in the solution. Whereas the life time for PD 1 was decreased by 2.75 times under the same conditions. This can be explained as result of the increased charge transfer process from the dye to the semiconductor due to better contact of functionalized molecules with titanium dioxide nanoparticles.<sup>[9b]</sup>

**Table 2** Spectral-luminescent properties\* of PDs on the surface of porous TiO<sub>2</sub> films.

Sample, wt%	<sup>a</sup> λ <sub>max</sub> , nm	D	<sup>f</sup> λ <sub>max</sub> , nm	I, a.u.	I/I <sub>0</sub>	τ <sub>fl</sub> , ns
<b>PD 1</b>						
Solution	640	–	655	–	–	1.10
TiO <sub>2</sub>	648	0.67	663	53	–	0.40
Ag@TiO <sub>2</sub> 0.5%	648	0.69	660	84	1.59	0.40
Ag@TiO <sub>2</sub> 1.0%	648	0.71	657	75	1.41	0.50
Ag@TiO <sub>2</sub> 2.0%	648	0.9	663	54	1.02	0.63
<b>PD 2</b>						
Solution	646	–	663	–	–	1.90
TiO <sub>2</sub>	655	1.03	668	23	–	0.62
Ag@TiO <sub>2</sub> 0.5%	655	1.09	670	58	2.5	0.74
Ag@TiO <sub>2</sub> 1.0%	655	1.04	671	42	1.82	0.70
Ag@TiO <sub>2</sub> 2.0%	655	1.00	674	30	1.30	0.70

\* <sup>a</sup>λ<sub>max</sub> – maximum in absorption spectra, <sup>f</sup>λ<sub>max</sub> – maximum in fluorescence spectra, D – optical density in <sup>a</sup>λ<sub>max</sub>, I – fluorescence intensity, τ<sub>fl</sub> – fluorescence lifetime.

As plasmon Ag NPs were added to the TiO<sub>2</sub> film, an enhanced fluorescence of PDs was registered. Moreover, the maximum increase in intensity was recorded at a concentration of Ag@TiO<sub>2</sub> NPs, equal to 0.5 wt%. The plasmon-enhancement of the polymethine's fluorescence,  $I/I_0$ , is greater for functionalized PD 2. In particular, the maximum values of  $I/I_0$  were equal to 1.6 and 1.9, for PD 1 and 2, respectively. Meanwhile there were no noticeable changes in optical density (3–5%) of dyes.

This increase in the dyes fluorescence intensity could be the result of the growth of the radiative transition between excited and ground state of dye molecules. As the optical density of the molecules was almost unchanged, the excitation rate of molecules remains almost the same. However, at the growth in the radiative decay rate of S<sub>1</sub>-state of dye, usually the decreasing in the fluorescence lifetime is observed. As seen from the Table 2,  $\tau_{fl}$  of PDs show the increasing upon the growth of Ag@TiO<sub>2</sub> NPs concentration in the films.

The observed trend may be the result of an increase in the efficiency of fluorescence with a simultaneous weakening of the nonradiative deactivation of the S<sub>1</sub> state of the PDs molecules.<sup>[13a, 18]</sup> The second case for the increase in the dye fluorescence lifetime is the reverse energy transfer from Ag@TiO<sub>2</sub> NPs to the dye molecule, as was shown in the work of Ref.<sup>[14]</sup> The authors showed that in the case of the close arrangement of the dye and plasmon NPs, along with the quenching of the dye fluorescence by energy transfer to Ag NPs, a reverse process is also possible, which is delayed in time and leads to an increase in the dye fluorescence lifetime.

For PDs, the weakening in nonradiative deactivation of the S<sub>1</sub> state can occur due to a decrease in the main channel of deactivation of the excited state – photoisomerization around the bonds of the polymethine chain.<sup>[19]</sup> Its decrease on the surface of TiO<sub>2</sub> films is logical due to an increase in the structural rigidity of the PDs molecule on its surface. Since

the rigidity of functionalized PD 2 increases more than that of PD 1, it can be expected that the nonradiative constant decreases more strongly for the first dye than for the second. Hence,  $\tau_{fl}$  for PD 2 should be increased more than for PD 1. However, we have the opposite picture (Table 2). In particular, in the presence of Ag NPs,  $\tau_{fl}$  increased by 1.6 times and 1.15 times for PD 1 and 2 respectively. It proves the second mechanism.

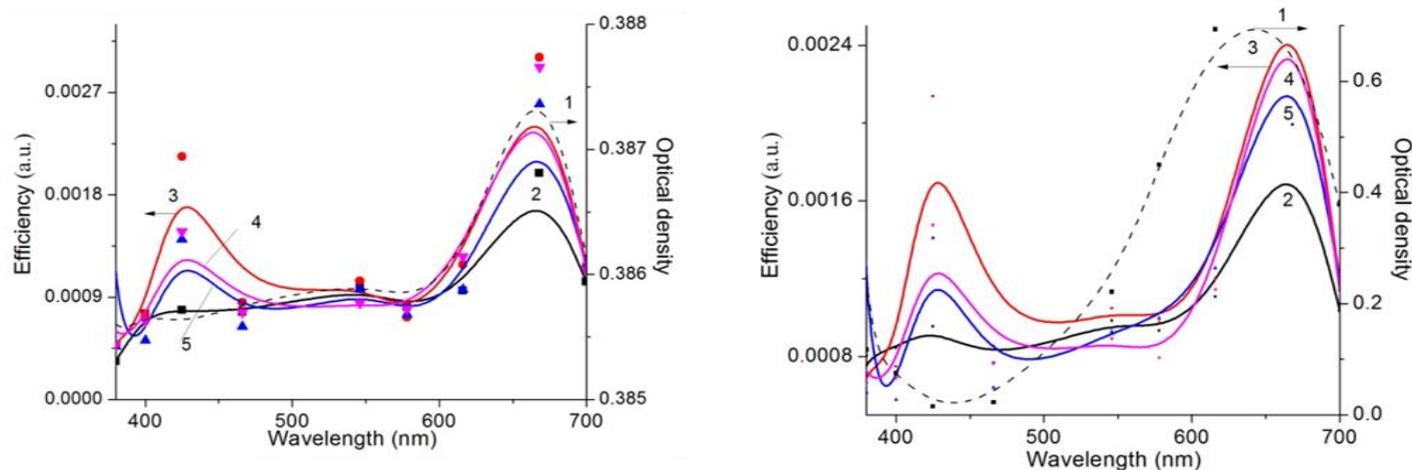
It is possible that the process of reverse energy transfer from Ag@TiO<sub>2</sub> NPs to PD 1 is more efficient due to the absence of bulk sulfonate groups in it, due to which PD 1 can approach the plasmon NPs at a closer distance. The effect of an increase in the fluorescence lifetime of merocyanine dye molecules near the surface of Ag NPs was also observed in Ref.<sup>[20]</sup>

The photovoltaic parameters of polymethine sensitized solar cells are presented in Table 3, where:  $J_{sc}$  – short circuit current density values,  $V_{oc}$  – open circuit voltage,  $FF$  – fill factor,  $\eta$  – cell efficiency.

Solar cell, sensitized with PD 1, has a low efficiency, which is due to the low value of the short circuit current of the cell. However, as Ag@TiO<sub>2</sub> NPs were added to the film, there was 2 times increase in the efficiency of the cell. As can be seen from the table, this is primarily due to an increase in the values of  $J_{sc}$ . For solar cells sensitized with PD 2 has higher cell efficiency.

The addition of 0.5 – 1 wt% of Ag@TiO<sub>2</sub> NPs to the TiO<sub>2</sub> film leads to an increase in solar cell efficiency by 15 – 20% for functionalized dyes, which is related to the increase of  $J_{sc}$  value. An increase in the concentration of Ag@TiO<sub>2</sub> NPs has a smaller effect on the efficiency of photoconversion of incident light by a solar cell.

The change in  $J_{sc}$  directly indicates an increase in the number of charge carriers in the solar cell. The growth in charge carriers may be due to the expansion of the spectral sensitivity of solar cells in the presence of Ag@TiO<sub>2</sub> nanostructures (Fig. 3).



**Fig. 3** The dependence of spectral sensitivity of solar cells sensitized by PD 1 (a) and PD 2 (b) via concentrations of Ag@TiO<sub>2</sub> NPs, wt%: 2 – 0; 3 – 0.5; 4 – 1; 5 – 2. Curve 1 – normalized absorption spectra of PD on the TiO<sub>2</sub>.

**Table 3** Photovoltaic parameters of DSSC based on PDs at various concentrations of Ag@TiO<sub>2</sub> NPs.

The concentration of NPs TiO <sub>2</sub> @Ag, wt%	$J_{sc}$ , mA/cm <sup>2</sup>	$V_{oc}$ , mV	$FF$	$\eta$ , %
<b>PD 1</b>				
0	0.11	375	0.15	0.06
0.5	0.18	416	0.20	0.15
1.0	0.11	375	0.16	0.07
2.0	0.11	304	0.15	0.05
<b>PD 2</b>				
0	3.56	350	0.14	1.74
0.5	3.94	354	0.15	2.09
1.0	3.30	349	0.15	1.72
2.0	3.00	349	0.14	1.47

A solar cell with **PD 1** is more sensitive to photoirradiation in the wavelength range from 600 to 700 nm (Fig. 3a). In this case, the maximum spectral sensitivity exhibits at 660 – 670 nm. Comparing the obtained curve with the absorption spectrum of **PD 1** on the TiO<sub>2</sub> surface, it was found that they coincide in shape.

An increase in the spectral sensitivity of the solar cell was noticed with addition of Ag@TiO<sub>2</sub> NPs to the bulk of a TiO<sub>2</sub> film. At the same time, a band in the region of 400 – 450 nm was detected, which was absent in the spectra of PD 1 without silver NPs. The maximum of this short-wavelength band was registered at 420 nm, which corresponds to the absorption band of plasmon Ag NPs. Similar data were obtained for semiconductor films sensitized with functionalized **PD 2** (Fig. 3b, Table 4).

**Table 4** Spectral sensitivity of DSSC based on PDs in the absence and presence of Ag@TiO<sub>2</sub> NPs.

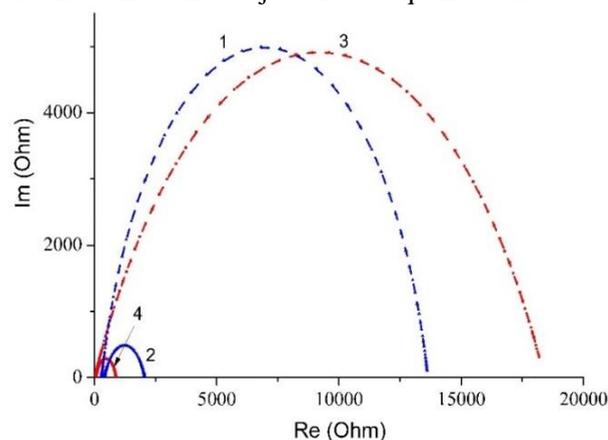
Sample	Spectral sensitivity, a.u. $\times 10^{-4}$	
	420 nm	670 nm
PD 1/TiO <sub>2</sub>	9.5	20.0
PD 1/TiO <sub>2</sub> +Ag@TiO <sub>2</sub> , 0.5 wt%	20.0	26.0
PD 2/TiO <sub>2</sub>	7.9	19.9
PD 2/TiO <sub>2</sub> +Ag@TiO <sub>2</sub> , 0.5 wt%	21.0	30.1

It should be noted that the spectral sensitivity, as well as the efficiency values at various wavelengths, is about 15% higher for **PD 2** than for **PD 1**. This could be the result of a larger number of **PD 2** molecules on the TiO<sub>2</sub> surface due to the anchor groups in the dye molecule. Since the dyes absorb light in close spectral ranges, the spectral sensitivity curves for **PD 1** and **2** are similar.

Moreover, the growth in the efficiency of DSSC with the dyes **1** and **2** is the result of an increase in the charge-transport characteristics of TiO<sub>2</sub> films with the addition of “core@shell” plasmon nanostructures (Fig. 4, Table 5).

Under the plasmon effect of Ag@TiO<sub>2</sub> NPs, the charge transfer resistance  $R_k$  associated with the recombination of an electron and a hole was decreased significantly. Parameter  $R_k$  was decreased by 8.2 times for **PD 1**, for **PD 2** – by 22.4

times in the presence of plasmon NPs. It leads to an increase in the charge-transport characteristics of semiconductor films, which can be expressed in the growth of charge carriers reaching the counter electrode. This is also evidenced by the growth of  $\tau_{eff}$ . Due to this the concentration of charge carriers grows and results in the deactivation of traps. This increases the part of photoelectrons reaching the counter electrode as it was shown in Refs.<sup>[11]</sup> It is possible that there are other factors that will be the subject of subsequent studies.

**Fig. 4** Impedance spectra of solar cells, sensitized by PDs **1** (1,2) and **2** (3,4) in the presence (2,4) and without (1,3) of Ag@TiO<sub>2</sub> NPs**Table 5** Electrotransport parameters of solar cells sensitized by PDs.

Sample	$R_k$ , Ohm	$R_w$ , Ohm	$\tau_{eff}$ , ms
PD 1/TiO <sub>2</sub>	13346	294.2	0.37
PD 1/TiO <sub>2</sub> +Ag@TiO <sub>2</sub> , 0.5 wt%	1635	419.0	2.68
PD 2/TiO <sub>2</sub>	18392	11.4	0.10
PD 2/TiO <sub>2</sub> +Ag@TiO <sub>2</sub> , 0.5 wt%	821	66.0	1.93

#### 4. Conclusions

The absorption and fluorescence bands of the studied PDs are located practically in the same spectral range of 500 – 800 nm with the maxima at 640 – 650 nm for absorption and 655 – 660 nm for fluorescence. A similar shape of the dyes

spectra due to the fact that they have almost the same chromophore.

During the adsorption of PDs molecules on the surface of TiO<sub>2</sub>, not only was a red shift (~10 nm) and noticeable broadening of the absorption bands were observed. Along with this, there is also a quenching of fluorescence and a decreasing in the lifetime of the excited state of PDs 1 and 2. Moreover, the efficiency of electron transfer to a semiconductor is much greater for a dye with functional groups. Thus, for PD 2,  $\tau_{fl}$  on the TiO<sub>2</sub> surface decreased by 3 times in comparison with  $\tau_{fl}$  in solution. Whereas for PD 1  $\tau_{fl}$  was decreased by 2.75 times under the same conditions. This can be explained by the presence of anchor sulfonate groups in the structure of dye 2. Those molecules are in closer contact with titanium dioxide nanoparticles that results in the growth in the number of electrons injected from PD to TiO<sub>2</sub>.

In the presence of Ag@TiO<sub>2</sub> NPs at a concentration of 0.5 wt%, a plasmon-enhanced fluorescence of dyes was observed in the TiO<sub>2</sub> film. The growth on 60 – 90% in the fluorescence intensity was observed. Moreover, for functionalized molecules, this effect is greater. It is likely that the observed increase in the intensity of the dye's fluorescence is associated with an increase in the radiative rate of dye molecules from S<sub>1</sub> to S<sub>0</sub> state. In this case, the excitation rate of molecules remains almost unchanged, because the optical density of the molecules increased slightly (on 3 – 5%). Consequently, the increase in fluorescence intensity can be associated with an increase in the rate constant of the radiation decay of dye molecules due to the process of reverse energy transfer from Ag@TiO<sub>2</sub> NPs to the dye molecule, which is confirmed by the data on the value of  $\tau_{fl}$  of PDs. In particular, in the presence of Ag NPs, the  $\tau_{fl}$  of PD 1 increased 1.6 times, for PD 2 – by ~1.2 times. At the same time, weakening in the nonradiative deactivation of the S<sub>1</sub> state also possible, however, this process makes the least contribution.

Comparing the influence of functional groups in the structure of the dye on the efficiency of generation of charge carriers in the solar cell, it can be noted that the efficiency of DSSC with PD 2 (1.74%) is higher than for PD 1 (0.06%). Taking into account that the amount of loaded dye for all cells was the same, we can state that the presence of sulfonate groups in the dye molecule contributes to an increase in the efficiency of the solar cells due to closer contact with semiconductor particles.

An increase in the efficiency of solar cells sensitized by PDs by 2 and 1.2 times for PD 1 and 2, correspondingly, in the presence of plasmon nanostructures can be the result of an increased light harvesting of cells in wavelength range of 600 – 700 nm and its expansion in the region of short

wavelengths (400 – 450 nm). In this case, plasmon enhancement of fluorescence and sensitization of the semiconductor proceed more efficiently for functionalized dyes. Moreover, the growth in the efficiency of DSSC with the dyes 1 and 2 is the result of an increase in the charge-transport characteristics of TiO<sub>2</sub> films with the addition of “core@shell” plasmon nanostructures. The charge transport resistance decreased by 8.2 times for dye 1 and by 22.4 times for dye 2. This leads to the growth the part of photoelectrons reaching the counter electrode. This is also evidenced by an increase in the lifetime of nonequilibrium charge carriers in TiO<sub>2</sub> films with Ag/TiO<sub>2</sub> NPs by 7 and 19 times for PDs 1 and 2, respectively.

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### Availability of data and material.

Data available within the article or its supplementary materials

### Supporting information

Not applicable

### Conflict of interest

There are no conflicts to declare.

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### Author information



**Niyazbek Ibrayev** received degree of Candidate of Physical and Mathematical Sciences in 1984 from Lomonosov Moscow State University, Russia. The degree of Doctor of Physical and Mathematical Sciences he obtained in the 1998 in the Institute of Physics and Technology, Kazakhstan. At present N. Ibrayev is the Professor at the Department of Physics and nanotechnologies of Buketov Karaganda University, Karaganda, Kazakhstan. Niyazbek Ibrayev is the head of the Institute of Molecular Nanophotonics of Buketov Karaganda University. Research interests: condensed matter physics, nanophotonics, nanoplasmonics, solar energy.



**Gulden Omarova** is the 3<sup>rd</sup> year PhD student under the supervision of Prof. Ibrayev N. and Prof. N. Nuraje at the Institute of Molecular Nanophotonics of Buketov Karaganda University, Karaganda, Kazakhstan. She obtained master's degree in 2005 from abovementioned University. Her current research focuses on studying of plasmon effect on photonics of polymethine dyes and its using in the photovoltaic and quantum electronics.



**Evgeniya Seliverstova** obtained PhD degree in 2014 from Buketov Karaganda University, Karaganda, Kazakhstan. She is currently working as senior researcher in the Institute of Molecular Nanophotonics of Buketov Karaganda University. Her research interests include

the dynamics of electronic excitations in organic nanostructures, photonics, plasmonics and carbon nanostructures.



**Alexander Ishchenko** is the Doctor of Chemical Sciences, PhD, Professor of Organic Chemistry. He is the Corresponding member of the National Academy of Sciences of Ukraine. Currently he is the head of the department of Color and Structure of Organic Compounds at the Institute of Organic Chemistry, National Academy of Sciences of Ukraine. Additional information could be found via link <http://ioch.kiev.ua/institute/research-departments/colour-and-structure-of-organic-compounds-department>.



**Nurxat Nuraje** received his PhD degree from CUNY in 2008. He was a postdoctoral associate in the Department of Materials Science and Engineering at MIT from 2008 to 2013 and a research scientist at MIT from 2013 to 2015. Then, he joined the chemical engineering department of Texas Tech University as an Assistant Professor starting from January of 2015. On August 26th of 2019, Dr. Nuraje started associate professorship position in the department of chemical and materials engineering of Nazarbayev University (NU) and is leading a NU Research Lab- Advanced Functional Materials & Device. During his PhD study, he was awarded the “Graduate Student Silver Medal” by the Materials Research Society (MRS) and the “Rose Kfar Rose” award by CUNY. In 2015, due to his outstanding researches in nanoscience, he was selected as the winner of the “Joseph Wang Award” by Cognizure organization. Dr. Nuraje has been awarded US Air Force Summer Faculty Fellowship for the years of 2017, 2018 and 2019, and was named one of the 2018’s RSC emerging investigators by Journal of Materials Chemistry A. In 2017, for his excellent performance in teaching, Dr. Nuraje was recognized as the most influential faculty member by college of engineering of Texas Tech University. So far, he has published more than 70 peer reviewed journal articles and 7 book chapters. As a primary editor, he published the RSC book- “Green Photoactive Nanomaterials: Sustainable Energy and Environmental Remediation”. At present, he serves as Editorial board members of three journals which are Materials Science in Semiconductor Processing (Elsevier), Journal of Experimental Science (Francis &

Taylor), and Advanced Composites & Hybrid Materials (Springer). As a guest editor, he organized two special issues. One is “Photoactive Nanomaterials” for the Journal –Nanomaterials. The second one is “Functional Green Nanomaterials” for the journal- Nanoscience and Nanotechnology—Asia (Bentham Science). He has served as chair/co-chair for four technical sessions in AICHE national meeting, and grant reviewers for US NSF, ACS PRF, National Center of Science and Technology Evaluation (Kazakhstan), and National Science Center of Poland. Dr. Nuraje’s research interests are primarily in nanomaterials and polymeric materials. Specifically, his goal is to explore the physical and chemical properties of new functional materials and understand their “bottom-up” assembly and formation into hierarchical structures with the goals of discovering new fundamentals and bringing about breakthroughs in solar energy conversion, environmental remediation, and oil recovery.

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