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Laser Irradiation as a Tool to Control the Resonance Energy Transfer in Bacteriorhodopsin–Quantum Dot Bio-Nano Hybrid Material

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Abstract

Bacteriorhodopsin (BR) is a natural photosensitive protein which can be considered promising in photovoltaics and optoelectronics because of its ability to produce a pronounced electrochemical response and controllably change its absorption spectrum under light excitation. However, its applicability is limited by its narrow absorption spectrum and low values of the absorption cross sections. Semiconductor quantum dots (QDs), which have high one- and two-photon absorption cross-sections in a UV- and NIR spectral regions, respectively, can significantly improve the light sensitivity of BR by means of Förster resonance energy transfer (FRET) from QD to BR. In this work, we demonstrate the possibility to control the efficiency of FRET from QD to BR within electrostatically bound complexes of QD and purple membranes (PM) containing BR. We show that laser irradiation of QDs at different wavelengths leads to distinct changes (rise or decrease) of QD luminescence quantum yield (QY) without changing of QD structure. Such photo-induced changes in the QY of QD lead to a corresponding change in the efficiency of FRET. We have estimated efficiencies of FRET from QD to BR in the PM complexes composed of irradiated and non-irradiated QDs and found the increase in FRET efficiency with irradiated QDs.

1. Introduction

Bacteriorhodopsin (BR) is a unique light-sensitive protein known for its ability to produce a pronounced electrochemical response to irradiation. The changes in the protein's absorption profile during photochemical transformations allow one to create optical logic gates based on BR. Owing to these properties, BR is a promising material for applications in optoelectronics [1]. However, the spectral region in which BR effectively absorbs light is limited to the band with a maximum at 568 nm, whereas

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its excitation in the UV, blue, and NIR spectral regions cannot be achieved. Semiconductor quantum dots (QDs) is fluorescent nanocrystals promising in the field of photovoltaics, optoelectronics and biosensing [2], which have high one-photon and two-photon absorption cross-sections in a UV- and NIR spectral regions, respectively, can significantly improve the light sensitivity of BR by means of Förster resonance energy transfer (FRET) from QD to BR [3–11]. In turn, the high work efficiency of the QD-BR nano-bio hybrid material implies a large number of FRET elementary actions from QD to BR per time unit, which is in strong correlation with the QDs' excited state population. The high intensity of laser irradiation makes it possible to turn a significant part of QDs ensemble into excited state and provoke, at the same time, various irreversible photo-induced processes leading to alteration of the QDs optical properties [12]. Therefore, the study of the effect of high-intensity laser irradiation on the FRET process inside the QD-BR nano-bio hybrid material is an important task that allows one to select the operation conditions for this material.

2. Theory

FRET is nonradiative dipole-dipole energy transfer between a donor in an excited state and an acceptor in its ground state [13]. The efficiency of FRET (E) is the number of the energy transfer events per donor excitation events. It can be determined as:

$$E = \frac{n_A R_0^6}{n_A R_0^6 + r^6}, \tag{1}$$

where R_0 is the Förster distance, r is the distance between the donor and acceptor, and n_A is the number of acceptors accessible for energy transfer from the donor. Förster distance (R_0), defined as the distance between the donor and acceptor at which the FRET efficiency is 50%:

$$R_0^6 = \frac{9000(\ln 10) Q_D \kappa^2}{128\pi^5 N n^4} J(\lambda), \tag{2}$$

where Q_D is the donor quantum yield, κ^2 is the transition dipole orientation factor, N is Avogadro's number, n is the refractive index of the medium, and $J(\lambda)$ is the normalized overlap integral between the donor luminescence spectrum and acceptor absorption spectrum. In the experiment the efficiency of FRET is determined by the following expression [13]:

$$E = 1 - \frac{I}{I_0}. \tag{3}$$

3. Materials and methods

We used samples of CdSe/ZnS/CdS/ZnS core/multishell QDs synthesized according to the procedure from [2]. As a radiation source, we used the second (532 nm), third (355 nm) and fourth (266 nm) harmonics of a YAG: Nd^{3+} - pulse laser with a repetition rate of 10 Hz and pulse energy 0.1 mJ or second harmonic (395 nm) of femtosecond laser Tsunami with repetition rate 80 MHz, pulse duration 60 fs and pulse energy 0,1 nJ. During irradiation 1,5 ml of QD solution in quartz cuvette was continuously mixed with a magnetic stirrer.

4. Results and discussion

In our previous works we have studied the efficiently FRET in electrostatically bounded complexes of QD and purple membranes (PM) containing BR under one- and two-photon laser excitation [7-9, 14]. During such experiments we have found that laser irradiation of QDs leads to an increase in luminescence intensity, while absorption spectra remained unchanged, what indicates a change in fluorescence quantum yield (QY) of QD. As can be seen from Figure 1A, irradiation of QDs solution by a femtosecond laser at wavelength 395 nm leads to increase of luminescence intensity of QDs by a factor of 1.25 when the number of absorbed photons per particle reaches 10^4. On Figure 1B one can see the absorption spectra of irradiated and non-irradiated QDs. This change in the QY of QD can affect the FRET efficiency within the complexes of QDs and PM.

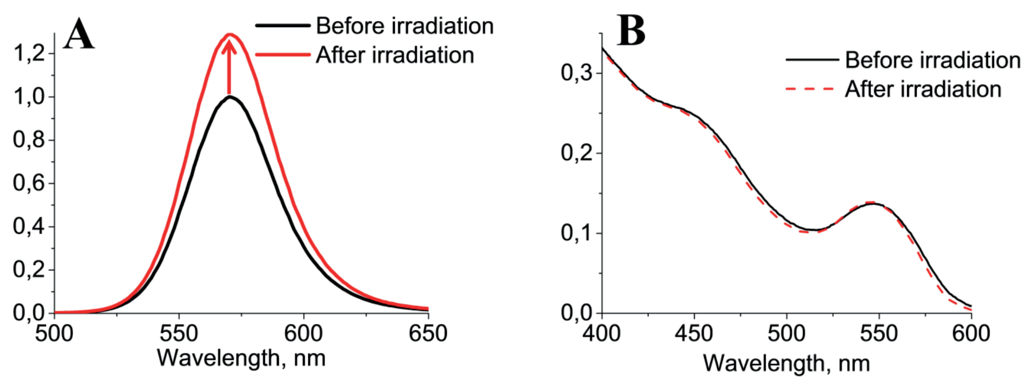

Figure 1: A – an increase in fluorescence intensity of QD after irradiation at a wavelength of 395 nm (absorbed dose of 10^4 photons per particle). B - absorption spectra of QDs before and after irradiation.

To estimate this effect we have prepared aqueous solution of complexes of QD with PM, as in [14]. We have measured FRET efficiency in this system using equation (3), and found its value to be 30%. Using the previously calculated values of Förster distance

[14] and the FRET efficiency obtained from current experiment, we estimated the distance between the donor and the acceptor, which was about 8,4 nm. Using equations (1) - (2), we estimated FRET efficiency with parameters of QD after irradiation, and the absolute increase in the FRET efficiency with irradiated QD should be 7%, as can be seen from Figure 2. Then we measured the FRET efficiency from irradiated QDs to BR in QD-PM complexes and experimentally found that it was 37%, which is 7% more than in the system with non-irradiated QDs and confirmed by our estimates. Thus, on the basis of these results, we propose a method for increasing the efficiency of FRET from QD to BR within the nano-bio hybrid complexes of QD-PM.

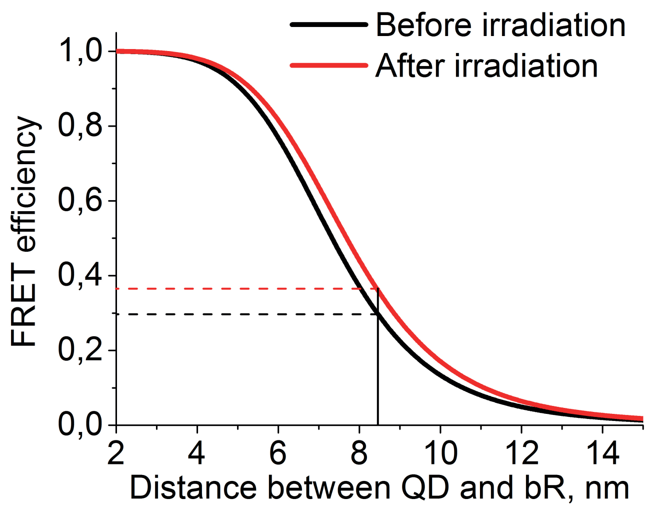

Figure 2: Dependence of FRET efficiency on the distance between QD and BR before and after irradiation.

In order to control the efficiency of resonance energy transfer in a hybrid material based on QD and BR, we have studied in detail the changes of the optical properties of QDs as a function of the irradiation wavelength and the number of photons absorbed per particle, and found that irradiation at different wavelengths affects the QY of QDs in different ways (Figure 3). Under 266 nm irradiation we observed a drop in QY, as in our previous works [9, 15, 16]. At the wavelengths of 355 and 532 nm, there was an correlating increase in QY with an increase in the dose of absorbed energy. In all cases the absorption spectra remained unchanged, which indicates that the QD structure is not altered and no precipitation has occurred. These results show that a flexible control of FRET efficiency is possible in the QD-BR system without changing their structure by use of only light irradiation. Specifically, it is possible to increase or decrease FRET efficiency by appropriate choice of the irradiation wavelength and the dose of absorbed photons.

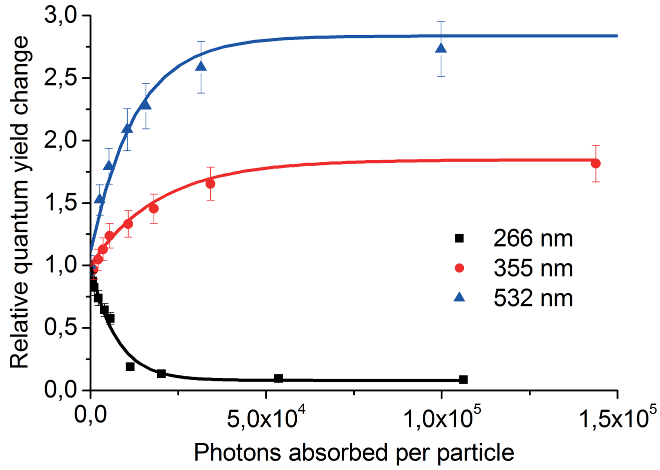

Figure 3: Changes in the QY upon irradiation at different wavelengths.

5. Summary

Earlier, we have shown that irradiation at a wavelength of 266 nm leads to a drop in QD QY and can be used to reduce the FRET efficiency from QD to BR in QD-PM complexes. Here we propose a method to increase the QY of QDs and, correspondingly, to increase in the efficiency of FRET from QD to BR after laser irradiation of QDs. These experimental results not only allow one to optimize the operating conditions for nano-bio hybrid material based on QDs and BR, but can also be used to control the efficiency of FRET from QD to BR inside the QD-PM complexes without affecting their structure and geometry.

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