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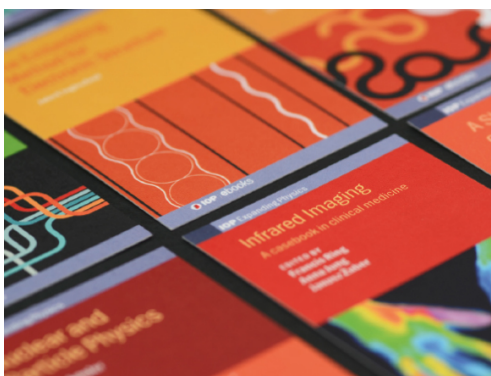
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Photoinduced modification of quantum dot optical properties affects bacteriorhodopsin photocycle in a (quantum dot)–bacteriorhodopsin hybrid material

V A Krivenkov^{1,2}, D O Solovyeva¹, P S Samokhvalov¹, K I Brazhnik¹, G E Kotkovskiy^{1,2}, A A Chistyakov^{1,2}, E P Lukashev^{1,3} and I R Nabiev^{1,4}

¹Laboratory of Nano-Bioengineering, National Research Nuclear University MEPhI, Kashirskoye shosse 31, 115409 Moscow, Russian Federation

²Department of Micro- and Nanophysics, National Research Nuclear University MEPhI, Kashirskoye shosse 31, 115409 Moscow, Russian Federation

³Department of Biophysics, Moscow State University, Vorobyovy Gory, 119992 Moscow, Russian Federation

⁴Laboratoire de Recherche en Nanosciences, LRN-EA4682, Université de Reims Champagne-Ardenne, 51100 Reims, France

E-mail: vkrivenkov@list.ru

Abstract. A method for controlled changes in the radiative properties of quantum dots (QDs) in order to modulate the Förster resonance energy transfer (FRET) rate in nano-hybrid materials is proposed. The mechanism underlying the effect of QDs with optical properties modulated by UV laser irradiation on the photocycle of the photosensitive protein bacteriorhodopsin (bR) in its native purple membranes (PM) isolated from *Halobacterium salinarum* has been studied. The irradiation leads to a twofold decrease in the QD fluorescence quantum yield without changes in the extinction spectrum or the position or shape of the fluorescence spectrum. The bR photocycle is accelerated, which has been shown to be related to the changes of the surface potential of PM upon formation of their complexes with QDs.

1. Introduction

The photosensitive protein bacteriorhodopsin (bR) [1], a photosensitive membrane protein from purple membranes (PMs) of *Halobacterium salinarum*, is a promising potential component of photovoltaic nano–bio hybrid structures [2] which utilizes as little as 0.1–0.5% of the total energy of the solar light optical spectrum [3]. The harvesting and utilization of solar energy by photosensitive proteins can be made substantially more efficient by complexing them with semiconductor nanocrystals or quantum dots (QDs), which are capable of absorbing light in the UV and visual spectral regions and passing the absorbed energy to the photosensitive proteins through the Förster resonance energy transfer (FRET) mechanism [4, 5]. It has been demonstrated that the transfer of additional energy to bR or photoreactive centers can increase the efficiency of proton transport by bR [4] and charge separation during photosynthesis [5]. It was also been shown that the integration of QDs into purple membranes (PMs) containing bR could accelerate the formation of the intermediate M-form of the bR photocycle, although the mechanism of this effect remained unknown [6].



This study was aimed at determining the mechanisms of QD effects on M-form of the bR photocycle. For this purpose, we directionally changed the QD optical properties by means of laser UV irradiation before their integration into PMs in order to estimate the possible contribution of the resonance energy transfer from QDs to bR into the acceleration of the formation of the bR M-form.

UV irradiation allows the FRET efficiency to be changed without affecting the structural organization of the nano-hybrid system. Radiation with a quantum energy greater than the QD band gap is known to cause a decrease in the quantum yield (QY), as well as a blue shift of the absorption and fluorescence spectra of the nanocrystals [7-9]. For preserving the QD structural integrity, the irradiation mode should be so selected that the nanocrystal QY is changed without altering the shape of their absorption spectra. The use of these UV-irradiated QDs could make it possible to modulate the FRET efficiency without affecting the structure of the QD-based nano-hybrid system and determine the mechanism of the QD effect on bR leading to accelerated formation of intermediate forms in the bR photocycle.

2. Theory

FRET is non-radiative energy transfer between donor chromophores in an excited state (D) and acceptor chromophores in their ground state (A) [10]. One of the key parameters determining the efficiency of FRET is the Förster radius (R_0), defined as the distance between D and A for which the FRET efficiency approaches 50%. It can be calculated from the intrinsic optical and spectral parameters of D and A:

$$R_0^6 = \frac{9000(\ln 10) Q_D \kappa^2}{128\pi^5 N n^4} J(\lambda) \quad (1)$$

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 D emission and A absorption. The normalized overlap integral is calculated as follows:

$$J(\lambda) = \int_0^{\infty} F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda \quad (2)$$

where F_D is the normalized emission of D, and ε_A is the molar absorption coefficient of A at the wavelength λ .

The FRET efficiency (E), which reflects the theoretical proportion of absorbed photons transferred to the acceptor at a given distance, can be determined using the following equation:

$$E = \frac{n_A R_0^6}{n_A R_0^6 + r^6} \quad (3)$$

where R_0 is the Förster radius, r is the distance between the donor and the acceptor, and n_A is the number of acceptors accessible for energy transfer from the donor.

3. Experimental

We use bR in its native purple membranes (PM) because the isolation of bR from PMs considerably decreases both the biochemical and thermodynamic stabilities of the protein. PMs were isolated from *H. salinarum* by the standard procedure [11]. The concentration of bR in solutions was measured by light absorbance at 570 nm (the bR molar extinction coefficient was $63000 \text{ M}^{-1} \text{ cm}^{-1}$). The changes in the bR light absorbance were measured using a laboratory flash-photolysis setup with the probing beam passing a double monochromator after excitation of the sample with a Nd-YAG laser (532 nm, 8 ns, 15 mJ).

A chloroform colloid solutions of CdSe/ZnS QDs synthesized as described in [12] and coated with trioctylphosphine oxide (TOPO) were exposed to UV laser irradiation (266 nm, 8 ns, 1 mJ) at a dose of about $1.5 \times 10^{-16} \text{ J}$ per particle. The TOPO concentration was about 1 mg/ml. The QDs extinction

spectrum, as well as the shape and position of their fluorescence spectrum, remained unchanged after the irradiation, while the QY was two times decreased.

The surface of both irradiated and nonirradiated particles was functionalized with PEG-OH [13] to make them water-soluble and stable in aqueous solutions. The fluorescence peak position of QDs after functionalization was 570 nm. The functionalized QDs were used to obtain the aqueous solutions of QDs, PMs, and their mixtures, the description of which is given in Table 1. The pH of all these solutions was 6.5. The fluorescence intensity and lifetime of the QDs water solutions were measured by means of a FLUOROLOG-3 spectrofluorimeter (Horiba Jobin Yvon) using the TCSPC option (Time-Correlated Single Photon Counting). The lifetimes (τ obtained from fluorescence and photopotential measurements) were evaluated by multiexponential fits and presented as average lifetimes (τ_{avr}) in all cases. The τ_{avr} value was calculated as the sum of the products of each τ value by the respective amplitude divided by the sum of all amplitudes.

Table 1. Samples used in experiments.

| | Molar concentration of QDs in solution, μM | Molar concentration of bR in solution, μM | QDs condition |
|-----------------|---|--|---------------|
| Sample 1 | 1,2 | - | nonirradiated |
| Sample 2 | - | 7,2 | - |
| Sample 3 | 1,2 | 7,2 | nonirradiated |
| Sample 4 | 1,2 | 7,2 | irradiated |

4. Results and discussion

In [6] was found that the integration of QDs into purple membranes (PMs) containing bR could accelerate the formation of the intermediate M-form of the bR photocycle. And this is particularly strong effect was observed for QDs with a fluorescence maximum at a wavelength of 570 nm, almost coinciding with the maximum of the bR absorption band. For such quantum dots FRET to bR is maximal because the overlap integral (equation 2) is maximal [11]. Therefore it is interesting to clarify the role of FRET in bR photocycle acceleration process. It can be done by UV laser irradiating which reduce the quantum yield of QDs without affecting the structure of the QD-PM nano-hybrid system. As follows from equation 1, the reduction in QDs quantum yield should reduce the Förster radius. As follows from equation 3, the reduction in Förster radius should lead to a decrease in FRET efficiency. If the FRET affects the kinetics of the bR M-form formation, then with a decrease in energy transfer efficiency the speed of bR photocycle also changes. We was studied the kinetics of the bR M-form in aqueous mixtures of PMs with both irradiated and non-irradiated QDs.

In order to demonstrate that FRET occurred in the aqueous mixtures of QDs and bR, we plotted the dependence of the nonradiative fluorescence quenching rate for QDs not exposed to UV irradiation on the amount of bR added to the solution (Fig. 1a). The nonradiative fluorescence quenching in QD solutions was estimated as:

$$F = 1 - \eta \frac{I}{I_0} \quad (4)$$

where F is the nonradiative quenching rate, I is the sample fluorescence intensity in the presence of bR, I_0 is the sample fluorescence intensity in the absence of bR, and η is a correction factor taking into account light energy reabsorption [14]. It has been shown [4] that FRET between the donor (QDs) and acceptor (bR) is the main nonradiative relaxation pathway in aqueous solutions of QDs and bR. Thus, data shown in Fig. 1a demonstrate that the FRET efficiency increases with increasing proportion of bR

in the QD–bR system. FRET in this system is also confirmed by a shorter average luminescence decay time in sample 3 compared to sample 1 (Fig. 1b).

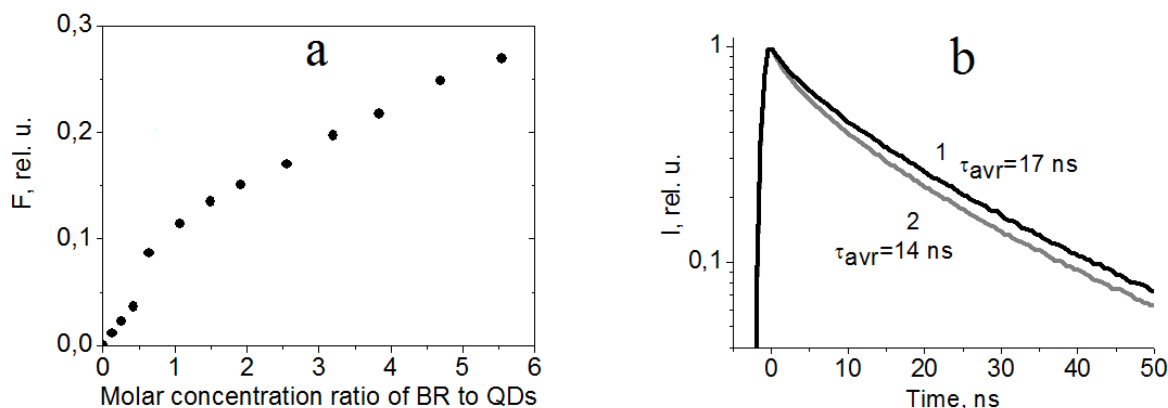


Figure 1. (a) Dependence of the nonradiative fluorescence quenching rate for QDs not exposed to UV irradiation on the bR-to-QD molar ratio in their mixed aqueous solution. (b) Changes in the fluorescence kinetics of QDs in the presence of bR (1 – nonirradiated QDs water solution; 2 – water mixture of nonirradiated QDs and PMs).

Figure 2a shows the kinetics of the formation of the bR M form (the dependence of the absorbance at a wavelength of 410 nm on time) in the experimental samples 2–4. As can be seen in the figure, this kinetics was the same for the bR–QD mixture with a twofold decreased QY and the mixture of bR and nonirradiated QDs. The average times of the absorption increase are $60 \pm 5 \mu\text{s}$ for PM suspensions and $40 \pm 3 \mu\text{s}$ for all bR–QD mixtures; the average times of the absorption decrease are 4.9 ± 0.4 ms and 3.3 ± 0.2 ms, respectively. Therefore, we may conclude that FRET between bR and QDs does not affect the kinetics of the formation of the bR M-form.

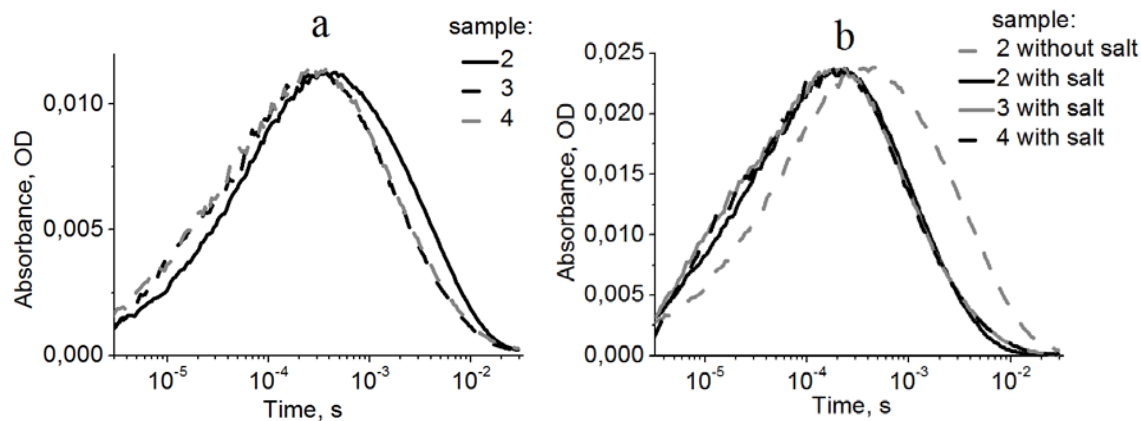


Figure 2. (a) Kinetics of the formation of the bR M-form in samples 2 (PMs water solution), 3 (water mixture of nonirradiated QDs and PMs), and 4 (water mixture of irradiated QDs and PMs). (b) Kinetics of the formation of the bR M-form in samples 2, 3, and 4 with an increased NaCl concentration (100 mM) in comparison with sample 2 without increasing of NaCl.

In addition, we measured the kinetics of the formation of the M form at an increased NaCl concentration in the solutions studied (100 mM; pH remained at 6.5), when charges on the PM surface were screened (Fig. 2b). The results showed that, at a high concentration of the salt, the kinetics of the formation of the bR M-form was the same in the presence and absence of QDs. The average times of the absorption increase and decrease are $37 \pm 3 \mu\text{s}$ and 1.77 ± 0.14 ms respectively for all samples with an increased NaCl concentration. On the other hand, an increased ionic strength accelerated the

formation and breakdown of the M-form; i.e., it had the same effect as the addition of QDs to PMs. Thus, the effect of QDs on bR may be accounted for by the modification of the PM surface potential in the QD–PM system.

5. Conclusion

We have developed a method for directional modification of the QD radiative properties in order to control the FRET rate in nano-hybrid materials. The mechanism underlying the effect of QDs with optical properties changed by UV laser irradiation on the photocycle of bR in PMs isolated from *Halobacterium salinarum* has been studied. The mode of laser irradiation has been so adjusted that it caused a twofold decrease in the QD luminescence QY without affecting either their extinction spectrum or the position or shape of their fluorescence spectrum. We have demonstrated that the accelerated formation of the bR photocycle M-form intermediate is related to the changed PM surface potential in the QD–PM complexes rather than FRET between QDs and bR. The method developed offers new opportunities for studying QD-based nano-hybrid systems and makes it possible to improve the characteristics of light-harvesting and light-emitting devices in which these systems are used.

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