Quantum Dots for Enhanced Light Harvesting: Exploration of Energy Transfer from Semiconductor Nanocrystals to Photosynthetic Biological Complexes

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Abstract

The development of artificial systems that utilize solar energy is one of the most challenging goals of material sciences. Also, much of the current research effort in this field is directed towards self-assembled bio-monolayers and protein-based photonic devices [1].

Recently it was suggested that inorganic nanocrystals or quantum dots (QDs), which are able to collect light over a wide spectral window, may achieve significantly greater absorption than natural photo-bio-systems, and could thus be used to enhance the light-harvesting process [2]. These QDs may also be very efficient in excitation energy transfer [3]. This has led us to contemplate the development of novel hybrid materials in which light energy harvested by the QDs in the optical region may be transferred to the photo-active biosystems in order to enhance their efficiency.

Here I outline our recent achievements in development of two novel hybrid materials build from semiconductor QDs and photosensitive membrane complexes: - purple membranes (PM) from bacteria *Halobacterium salinarum* containing membrane protein bacteriorhodopsin (bR) [4], and photosynthetic reaction centers (RCs) purified from bacteria *Rhodobacter sphaeroides* [5].

bR is a single integral membrane protein incorporated within the purple membranes of bacteria *Halobacterium salinarum* where it forms tight trimers highly organized into the ultrastable two-dimensional crystal lattice with a unit-cell dimension of 6.2 nm. Upon illumination by light, bR undergo a cyclic sequence of photo-intermediates changing absorption in the blue-to-red region of optical spectrum. The high quantum efficiency of the initial bR state guarantees an efficient photoisomerization of the protein-linked bR chromophore (retinal), which is strongly absorbing light and located near to the centre of the PM, at a distance from both PM surfaces of nearly 2.5 nm.

Absorption of light by the retinal results in pumping the protons through the PM creating an electrochemical gradient which is then used by the ATPases to energize the cellular processes. High level of bR intra-membrane structural organization determines its long-term stability against thermal and photochemical degradation and makes PM the most promising bio-candidate for device applications where the energy conversion, photochromism, and photoelectrism are the inherent effects which may be employed.

Very recently we have optimized bR biological function through the engineering of a “nanoconverter” of solar energy based on semiconductor CdTe QDs tagged with the PM. These nanoconverters are able to harvest light from deep-UV to the visible region and to transfer additionally collected energy to bR via Förster resonance energy transfer (FRET) with nearly 100% efficiency leading to significant increase of efficiency of light-driven trans-PM proton pumping [5].

In similar approach we were able to integrate semiconductor QDs with the simplest and best understood photosynthetic RC found in purple bacteria (*Rhodobacter sphaeroides*). The RC is composed of cofactors (building blocks) arranged into two membrane-spanning branches. One of these branches is active in catalyzing electron transfer, however both branches are connected to a key element of the RC which is a dimer of BChl molecules, the so-called “special pair” (P or P870). In nature, a solar photon first creates an excitation in the RC and then this excitation moves towards P870, where the electron separates from the hole within 2–3 ps. Recently we demonstrated that that semiconductor QDs of selected PL wavelengths can be tagged with the RC in such a way that FRET from the QDs to the RC is realized. A nearly threefold increase in the rate of generation of excitons in the RC is demonstrated, and theoretical estimates predict even stronger enhancements, thus indicating that further optimization is possible [5].

Also our recent studies revealed that FRET-based improvement of the biological function of bacteriorhodopsin in the presence of QDs allows for strong wavelength-dependent enhancement of the nonlinear refractive index of bacteriorhodopsin .

In summary, we have demonstrated that QDs specifically immobilized on the surface of the photo-active bio-systems are able to play the role of a built-in light energy convertor by harvesting light which would not be absorbed efficiently by the bio-system alone (from UV to blue region). Semiconductor QDs were further demonstrated to be able to transfer the harvested energy via highly efficient FRET to this

complex biological systems. We have finally demonstrated a first proof-of-the-principle evidence that the bR being a part of engineered QDs-PM hybrid material is able to utilize the transferred by QDs additional energy to improve the efficiency of its biological function.
We believe that our results on the transfer of energy harvested by QDs to a RC are important, because they pave the way for the use of QDs as light-harvesting built-in antennae for artificial photosynthesis. In green plants the reaction center of Photosystem II has a charge-separation site very similar to that of the bacterial reaction center. Therefore, from a fundamental point of view, our results on efficient energy transfer from QDs to the bacterial RC offer interesting possibility for the utilization of QDs to enhance the efficiency of the photosynthetic biological function. It is worth mentioning that the enhancement of biological functions of natural photosynthetic systems, if realized, should have a strong impact on energy-related technologies.

References

[1] R.R. Birge, N.B. Gillespie, E.W. Izaguirre, A. Kusnetzow, A., A.F. Lawrence, D. Singh, Q.W. Song, E. Schmidt, J.A. Stuart, J.A., S. Seetharaman, K.J. Wise, J. Phys. Chem. B, **103** (1999) 10746.
[2] A.O. Govorov and I. Carmeli, Nano Lett., **7** (2007) 1642.
[3] T. Franzl, A. Shavel, A.L. Rogach, N. Gaponik, T. Klar, A. Eychmuller, J. Feldmann, Small, **1** (2005) 392.
[4] A. Rakovich, A. Sukhanova, N. Bouchonville, E. Lukashev, V. Oleinikov, M. Artemyev, V. Lesnyak, N. Gaponik, M. Molinari, M. Troyon, Y.P. Rakovich, J.F. Donegan, I. Nabiev, Nano Lett., **10**, (2010) 2640.
[5] I. Nabiev, A. Rakovich, A. Sukhanova, E. Lukashev, V. Zagidullin, V. Pachenko, Y.P. Rakovich, J.F Donegan, A.B. Rubin, A. O. Govorov, Angew. Chem. Int. Ed**., 49**, (2010) 7217.
[6] A. Rakovich, I. Nabiev, A. Sukhanova, V. Lesnyak, N. Gaponik, Y.P. Rakovich, J.F. Donegan, ACS Nano, **7** (2013) 2154

Figures

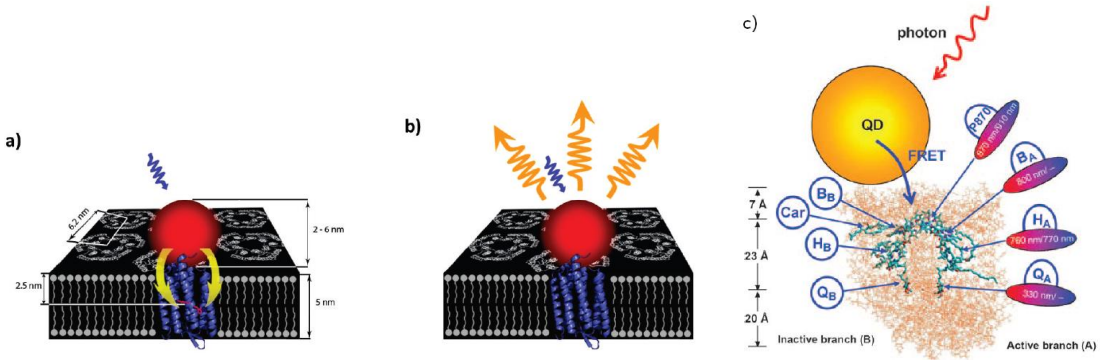

Fig. 1. Structural organization of purple membrane-QDs hybrid material and optical properties of bR and QDs. a) Photons are absorbed by the QDs immobilized on the surface of the PM containing bR. An exciton from the QDs is transferred via FRET to the bR. This energy transfer results in the strong quenching of the PL of QDs. For QDs complex with the “white membranes” (WMs: PMs with the extracted bR) – QDs immobilized on the surface of the WM do not transfer an exciton to the acceptor because this acceptor (bR) is absent (b). Panel c shows organization and functionality of a complex composed of the reaction center (from Rb. sphaeroides) and a QD; the diagram is given to scale. Active (A) and inactive (B) branches in the electron-transfer cofactor are shown. The positions of the absorption/photoluminescence maxima for the BChl special pair (P870), BChl monomer (B), bacteriopheophytine (H), and quinone (Q) are indicated for the active branch (A) only. Photons are absorbed by both the RC and the QD. An exciton from the QD is transferred to the RC by FRET. Car=carotenoid.