

Hybrid Materials Engineered from Bacteriorhodopsin and Semiconductor Quantum Dots or Metal Nanoparticles: What Nano Does with Bio?

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Semiconductor or metal nanocrystal self-assembly on, or their chemical attachment to, photosensitive biological systems (purple membranes of the bacterium *Halobacterium salinarum* or photosynthetic reaction centers) may strongly affect biological functions and cause plenty of interesting linear and non-linear photophysical effects on the nano-bio interface [1–3].

We report on the procedure of careful self-assembling of semiconductor fluorescent nanocrystals or “quantum dots” (QDs) [4] on the surface of a purple membrane (PM) of *H. salinarum* in a manner permitting Förster resonance energy transfer (FRET) from the QDs to retinal, the fluorophore of bacteriorhodopsin (bR), with an efficiency as high as 100% (Figure 1A) [5]. Additionally, we report on an enormous, wavelength-dependent enhancement of the nonlinear refractive index of wild-type bacteriorhodopsin in the presence of semiconductor QDs (Figure 1B). The effect is the strongest in the region immediately below the absorption edge of both constituents of this hybrid material and in samples that exhibit strong FRET. We have shown that enhancements of up to 4000% can be achieved by controlled engineering of the hybrid structure, including variation of the molar ratio between the constituents.

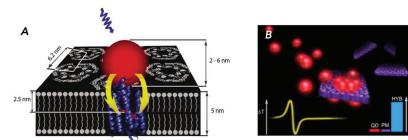


Figure 1 Self-assembly of colloidal semiconductor quantum dots (QDs, red spheres) and purple membranes (PMs, planar purple structures) in a solution: the two components are drawn to scale.

Panel A. A semiconductor nanoparticle assembled with a bacteriorhodopsin trimer on the PM surface and optically coupled with the retinal in order to achieve efficient FRET from the nanoparticle to the retinal. Adapted from Refs. 2 & 5.

Panel B. The nonlinear properties of QD-PM samples measured by the Z-scan technique: the yellow “butterfly” curve is a representative Z-scan curve. It has been found that, upon assembly of QD-PM complexes, the amplitude of the nonlinear refractive index (n_2) of the material is increased up to 4000% (as shown diagrammatically in the bottom right corner). Adapted from Ref. 6.

Finally, we have demonstrated that semiconductor or metal nanoparticles with different surface functionalities can be employed to control the parameters of the bR photocycle. We have shown that the lifetime of the intermediate M-form of the bR photocycle may be significantly increased when the PM is tagged with semiconductor or silver nanoparticles with desired surface charges. These new hybrid materials based on complexes of PMs with nanoparticles with unique photochromic, energy transfer, energy conversion and nanophotonic properties may be used in numerous optoelectronic applications [7]. The last but not least part of this report deals with the issues of nanomaterial toxicity resulting from the basic molecular mechanisms of interactions between nano- and biomolecular systems [8].

References

- [1] I. Nabiev, A. Rakovich, A. Sukhanova, E. Lukashev, V. Zagidullin, V. Pachenko, Y. Rakovich, J. F. Donegan, A. B. Rubin, A. O. Govorov, Fluorescent quantum dots as artificial antennas for enhanced light harvesting and energy transfer to photosynthetic reaction centers. *Angew. Chem. Intl Ed.* **49**, 7217–7221 (2010).
- [2] A. Rakovich, A. Sukhanova, E. Lukashev, V. A. Oleinikov, M. Artemyev, N. Gaponik, N. Bouchonville, M. Molinari, M. Troyon, Y. P. Rakovich, J. F. Donegan, I. Nabiev, Resonance energy transfer improves the biological function of bacteriorhodopsin within a hybrid material built from purple membranes and semiconductor quantum dots. *Nano Lett.* **10**, 2640–2648 (2010).
- [3] A. Rakovich, J. F. Donegan, V. A. Oleinikov, M. Molinari, A. Sukhanova, I. Nabiev, Yu. P. Rakovich, Linear and nonlinear optical effects induced by energy transfert from semiconductor nanoparticles to photosensitive biological systems. *J. Photochem. Photobiol. C: Photochem. Rev.* **20**, 17–32 (2014).

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- [4] P. Samokhvalov, M. Artemyev, I. Nabiev, Basic principles and current trends in colloidal synthesis of highly luminescent semiconductor nanocrystals. *Chemistry - A European Journal* **19**, 1534–1546 (2013).
- [5] N. Bouchonville, A. Le Cigne, A. Sukhanova, M. Molinari, I. Nabiev, Nano-biophotonic hybrid materials with controlled FRET efficiency engineered from quantum dots and bacteriorhodopsin. *Laser Phys. Lett.* **10**, 085901 (2013)
- [6] A. Rakovich, I. **Nabiev**, A. Sukhanova, V. Lesnyak, N. Gaponik, Yu. P. Rakovich, J. F. Donegan, Large enhancement of nonlinear optical response in a hybrid nanobiomaterial consisting of bacteriorhodopsin and cadmium telluride quantum dots. *ACS NANO* **7**, 2154–2160 (2013).
- [7] S. Yu. Zaitsev, D. O. Solovyeva, I. Nabiev, Monolayers of membrane proteins and hybrid nanostructures. *Adv. Coll. Interf. Sci.* **183–184**, 14–29 (2012).
- [8] A. Shemetov, I. Nabiev, A. Sukhanova, Nano-bio interactions of proteins and peptides with nanocrystals. *ACS NANO* **6**, 4585–4602 (2012).

