

Development of Nano-Bio hybrid material based on CdTe Quantum Dots and Bacteriorhodopsin protein for future technologies

Aliaksandra Rakovich¹, Alyona Sukhanova^{2,3}, Evgeniy Lukashev⁴, Nicolas Bouchonville³, Vladimir Oleinikov⁵, Mikhail Artemyev⁶, Nikolai Gaponik⁷, Michael Molinari³, Michel Troyon³, Yury P. Rakovich¹, John F. Donegan¹ and Igor Nabiev^{2,3,8}

¹ School of Physics and CRANN, Trinity College Dublin, Dublin 2, Ireland,

² Université de Reims Champagne-Ardenne, 51100 Reims, France,

³ CIC nanoGUNE Consolider, E-20018 San Sebastian - Donostia, Spain,

⁴ Department of Biophysics, Lomonosov Moscow State University, 119992 Moscow, Russian Federation

⁵ Shemyakin-Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences, 117987 Moscow, Russian Federation,

⁶ Institute of Physico-Chemical Problems, Belarusian State University, Minsk, Belarus

⁷ Technical University of Dresden, 01062 Dresden, Germany

⁸ IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain

rakovica@tcd.ie

Many technologies rely on the properties of “pure” semiconductor materials for operation. It has been proposed that future technologies will be based on hybrid materials, developed as a result of multidisciplinary studies combining the expertise in Physics, Chemistry and Biology. The interface between nano- and bio-technology, for example, has enormous potential to supply such hybrid materials.

Protein-based devices, for example has received considerable attention during the last few decades [1]. However, most of the light-sensitive proteins investigated for such purposes are not able to deal with the high energy of the UV photons [2]. In fact, most do not absorb UV photons at all, resulting in overall efficiencies of less than 1% [3]. Nanotechnology opens the way to improve the performance of these proteins. For example, semiconductor QDs are able to absorb photons over a wide spectral region [4] and then transfer the harvested energy to the chromophores of such proteins [5], while down converting the absorbed energy so the damage to the chromophores is minimized.

Here the development of a nano-/bio- hybrid material based on photochromic protein bacteriorhodopsin (bR) and CdTe semiconductor quantum dots (QDs) is described. CdTe QDs of carefully selected photoluminescence colours were attached to the purple membranes (PMs) of bacteria *Halobacterium salinarum* (containing photochromic membrane protein bacteriorhodopsin in its natural environment) by utilizing either electrostatic assembly or covalent conjugation (Fig.1).

When such hybrids were assembled electrostatically, QDs self-assembled on the surface of PMs in such a way that efficient Förster Resonance Energy Transfer (FRET) from QDs to bR was realized (Figs. 1 and 2). Results demonstrate significant quenching of QDs' PL due FRET from QDs (donors) to the protein-linked bR retinal (acceptor), with a corresponding decrease in the fluorescence lifetime of the QDs (Fig.2). Quenching of QDs PL in electrostatically-assembled complexes was found to be strongly dependent on both QDs' radii and their surface functionalization [7]. A 3-fold enhancement in FRET efficiency was observed when QDs were attached to PMs by chemical conjugation, due to a reduced donor-acceptor separation distance.

Most importantly, it was shown that attachment of QDs to PMs does not disturb the biological function of bR – the pumping of a proton (H^+) from cytoplasmic side to the extracellular side of the membrane did not cease. In fact, an upto 20% enhancement in its function was observed upon addition of QDs to the system.

The described nano-bio hybrid material, with advanced optical and biological functions, will allow the development of devices with unique electronic and photonic properties, paving the way to novel nanophotonic and photovoltaic applications.

References

- [1] Birge, R. R. *et al.*, J. Phys. Chem. B, **103** (1999) 10746-10766
- [2] Lao, K. & Glazer, A. N., Proc. Natl. Acad. Sci. USA, **93** (1996) 5258–5263
- [3] Archer, M. D., Barber, J. in Molecular to Global Photosynthesis (ed. Archer, M. D. & Barber, J.), Imperial College Press, London (2004) pp. 1-41
- [4] Resch-Genger, U., Grabolle, M., Cavaliere-Jaricot, S., Nitschke, R. & Nann, T., Nature Meth., **5** (2008) 763-775
- [5] Nabiev, I., Sukhanova, A., Artemyev, M. & Oleinikov, V. in Colloidal Nanoparticles in Biotechnology (ed. Elaissari, A.), Ch. **6**, Wiley & Sons Inc. (2008) 133-168
- [6] Nabiev, I., Efremov, R. G. & Chumanov, G. D., J. Biosciences, **8** (1985) 363-373
- [7] Rakovich, A., Sukhanova, A., Bouchonville, N., Molinari, M., Troyon, M., Cohen, J. H. M., Rakovich, Y., Donegan, J. F., Nabiev, I., Proc. of SPIE, **7366** (2009) 736620-1

Figures

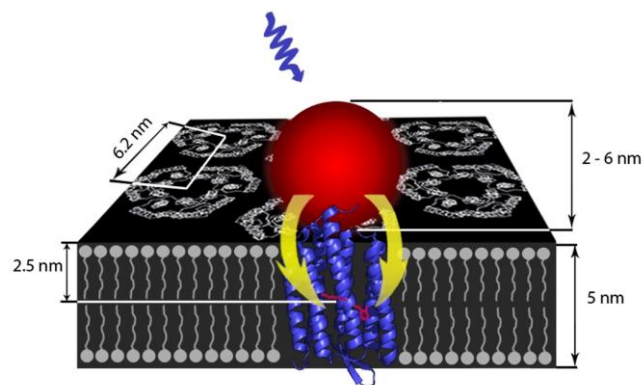


Figure 1 | Structure of QD-bR hybrid material. Each bR protein extends from one side of the purple membrane to the other, and contains one retinal molecule (shown in purple) [6]. Photon energy is absorbed by a QD immobilized on the surface of the PM. This energy is then transferred to the retinal by FRET mechanism, resulting in strong quenching of QDs' PL.

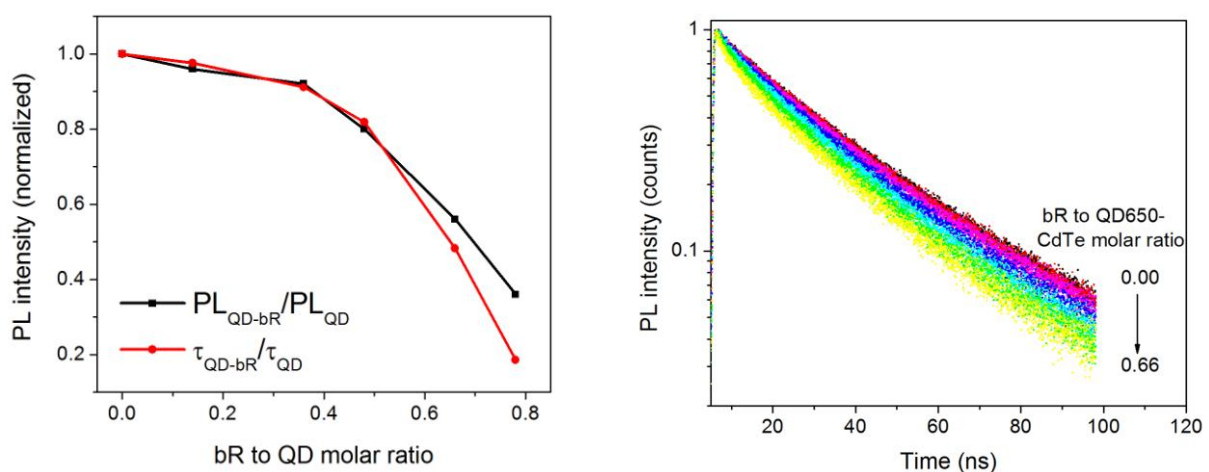


Figure 2 | Integrated photoluminescence and time-resolved photoluminescence decay as a function of bacteriorhodopsin to quantum dots molar ratios. Panel a: PL quenching of QD650 at different bR to QD molar ratios. There is very good agreement between the integrated PL measurements (—■) and lifetime data (—●), calculated as $1 - (FRET\ efficiency)$, suggesting that FRET is the main mechanism of quenching of QDs' PL. Panel b shows time-resolved data for bR-QD hybrids in which bR to QD molar ratios were changed from 0 to ~0.7.