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Invited Review

Linear and nonlinear optical effects induced by energy transfer from semiconductor nanoparticles to photosynthetic biological systems

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ABSTRACT

The development of new hybrid materials that can be integrated into current technologies is one of the most important challenges facing material scientists today. The purpose of this work is to review recent studies in one largely unexplored area of nanobiotechnology: the development of nano-bio hybrid materials that exploit Förster Resonance Energy Transfer (FRET) to enhance the functionalities of technologically promising photosynthetic biomaterials. One of very promising approaches is to employ semiconductor quantum dots having a broad absorption spectrum as nanoantennae coupled with the natural light-harvesting complexes of photosynthetic reaction centers. This system reveals great potential for the utilization of quantum dots in artificial photosynthetic devices. The second very useful functionality, which is discussed in this review, is the possibility to enhance the efficiency of the main biological function (proton pumping) of the protein bacteriorhodopsin using nonradiative energy transfer from quantum dots. Also recent studies revealed that FRET-based improvement of the biological function of bacteriorhodopsin in the presence of quantum dots allows for strong wavelength-dependent enhancement of the nonlinear refractive index of bacteriorhodopsin. These new hybrid bio-nanomaterials with exceptional light-harvesting and nonlinear properties will have numerous photonic applications employing their photochromic, energy transfer, and energy conversion properties.

Contents

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John Donegan received the PhD degree from University College Galway in 1986. He had post-doctoral periods in Lehigh University and in Max Planck Institut fuer Festkoerperforschung, Germany. He is Professor of Physics in Trinity College Dublin with an interest in the area of Photonics. He is a Principal Investigator in the CRANN and CTVR research centres in Trinity College. His research interests cover microcavity structures for linear and nonlinear optical interactions; Tunable diode lasers based on slotted Fabry-Perot structures; Integrated laser and optical modulator structures; CdTe nanocrystals and nanowires as novel photon emitters; Single and coupled Microsphere resonators. NV centres in diamond created through He-ion interactions.

Vladimir Oleinikov received his Ph.D. degree in Physics and Mathematics in 1980 from Moscow Physical Engineering Institute (MEPhI) and his D.Sci. degree from Shemyakin-Ovchinnikov Institute of Bioorganic Chemistry of the Russian Academy of Sciences (IBCh). He had postdoctoral period Iowa State University, USA and was appointed in academic staff in the Shubnikov Institute of Crystallography in 1986 and moved to IBCh in 1994. The area of his scientific interests include new nano-tools based on the semiconductor fluorescent nanocrystals and advanced biophysical approaches to study biological systems. Dr. Oleinikov is a Head of Laboratory of Molecular Biophysics in IBCh, and the Biophysics group Leader in Laboratory of Nano-Bioengineering in MEPhI. (www.ibch.ru and www.lnbe.mephi.ru/en/about).

Michaël Molinari received his Ph.D. degree in Condensed Matter Physics in 2002 from University of Nancy I in France. After a postdoctoral fellowship in the group of Pr. Fauchet in Rochester University (USA), he was nominated as Associated Professor of Physics in the University of Reims Champagne-Ardenne (URCA, France). Since 2010, he is Full Professor and deputy-director of the Laboratory of Research in Nanosciences (LRN EA4682) in Reims. Prof. Molinari is also deputy-director of the inter-university Technological Platform NanoMat' (University of Technology of Troyes - URCA, France). His main fields of research concern elaboration and characterization of semiconducting nanocrystals and nanowires and the development of original near-field microscopy techniques. In the last 5 years, he also participated to the development of bio-nano-hybrid materials and of their characterization by atomic force microscopy (www.univ-reims.fr/lrn).

Alyona Sukhanova graduated from the Russian State Medical University in 1993 with M.D. degree in medical biochemistry. She received her Ph.D. degree in molecular biology in 1998 from the Engelhardt Institute of Molecular Biology of the Russian Academy of Sciences. Dr. Sukhanova pioneered preparation and biofunctionalization of CdSe/ZnS QDs to make them water-soluble and biocompatible. She has developed the techniques of controlled thermodynamically driven QD self-assembly into one-, two-, and three-dimensional structures with desired optical properties and applications of these structures. Dr. Sukhanova has also published the results of the first application of QD–antibody conjugates to cancer diagnosis in situ in biopsies and demonstrated the potential of the use of QD-encoded microbeads in biosensing based on the FRET effect. In 2007 Dr. Sukhanova won the Distinguished Young Investigator Award from the Federation of European Biochemical Societies. She is one of the leading researchers in the LARGE European FP7 research program NAMDIATREAM developing photoluminescent nanoparticle-based reagents and diagnostic chips for high-throughput early diagnosis and treatment of cancer.

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1. Introduction

During millions of years of evolution photosynthetic organism have evolved complex apparatus to harvest, transfer and convert solar energy to produce high-energy molecules that fuel the organism [1]. The type and the number of photosynthetic systems (PS) used depends on the organism – plants and algae for example typically have two coupled PS (PSI and PSII). Anoxygenic organisms, which do not evolve oxygen, only have one PS [2]. For example, in purple bacteria *Rhodobacter sphaeroides* the conversion of solar energy into high-energy molecules *via* photosynthesis involves multiple steps [3]: First, solar photons are absorbed by antennae composed of pigment–protein complexes called the LH (light harvesting)-complexes (Fig. 1) and the energy is transferred in the form of an exciton, from the LH complexes to a reaction center (RC) (Fig. 1). The transfer is very fast and usually occurs within tens of picoseconds after absorption of a solar photon [2]. In the following step the exciton is spilt into constituent charges (an electron and a hole) by a dimer of two bacteriochlorophyll (B) molecules, the so-called special pair (P). Further, the charges are spatially separated through a series of photoinduced charge transfers along the chains of the reaction center to prevent immediate recombination [4]. Finally, the electrons are used in chemical transformations by a Cytochrome *bc1* complex and ATP-synthase to produce high-energy adenosine triphosphate (ATP) molecules that fuel the organism (Fig. 1).

However, the apparatus of photochemical conversion of harvested solar energy by an organism can also be very different from described above when optimization is needed for the specific environmental conditions. For example, in salt water where the concentration of the dissolved oxygen falls below what is needed for normal respiration, the bacteria *Halobacterium salinarum*, also known as *Halobacterium halobium*, have developed a system for energy conversion which consist of the bacteriorhodopsin (bR) protein coupled to ATP synthase (Fig. 2a), which is the simplest photosynthetic system known. Bacteriorhodopsin spans across a lipid bilayer membrane (purple membrane (PM) [5] and has