TALKS

Light-Reactions in Natural Photosynthesis

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Natural photosynthesis evolved as a modular system. Excitation energy is transduced into redox energy and membrane potential in the reaction center (RC), whose absorption cross section is enhanced by ~2 orders of magnitude by light-harvesting complexes (LHC). All RC are derived from a single ancestor, and use chlorophylls for light-induced charge separation. There exist, by contrast, a wide variety of LHC that use chlorophylls, carotenoids and/or bile pigments as chromophores to ensure successful competition for the prevailing light quantity and quality at any location. The various photosynthetic organism have, by exploiting this modularity, evolved to use light from 350 – 1050 nm as their primary source of free energy, and to cope with light intensities covering >6 orders of magnitude from full sunlight to near darkness. Individual organisms can acclimate their LHC/RC ratio and in some cases the absorption spectra of the LHC, and can adjust for temporal and spatial variations of the light.

Both RC and LHC work with quantum efficiencies Θ_Q >0.95. The energetic efficiency, Θ_E, is reduced by downgrading the excitation energy of the LHC to that of the absorption edge of the RC, and by a stepwise electron transfer; thereby ensuring directionality and avoiding potentially harmful charge recombination. Both systems have also evolved highly efficient safety mechanisms that minimize radiation damage of the highly phototoxic chlorophylls in case of system overload.

The above principles will be exemplified with selected RC and LHC, derived mainly from photosynthetic bacteria and algae, whose molecular structures are known at atomic resolution, and whose photophysics are explored at timescales down to femtoseconds by a combination of site-selective biochemical modifications and time-resolved spectroscopy. They biological concepts will be compared to technical approaches using single and tandem photovoltaic devices and light collection systems.

Translating Photosynthesis onto Gold Electrodes

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Photosynthesis is a biological process that takes place in cells consisting of the absorbance of solar photons and subsequent energy transfers and transformations into a fuel. As such, photosynthetic systems serve as a template for solar energy to fuel cells. The conversion reactions are carried out by proteins, biological polymers that fold into a specific shape. Often proteins are conjugated into complexes, fine-tuned to carry out a specific reaction. Photosynthetic solar energy conversion uses various types of protein-complexes that interact via weak electrostatic forces and are organized within a network. Such networks are interesting to investigate because they represent the essence of living matter, the ability to change organization in order to adapt in response to changes in the environment. The amount of knowledge and control of the photosynthetic process has become such that we can now start to integrate the photosynthetic process into devices as biosensors and solar to fuel cells. Here I discuss our recent efforts on interfacing the light-active protein complexes functionally onto gold surfaces. Light-harvesting systems that absorb light and transfer excited state energy can be oriented using engineered cysteine residues. Reaction Centers, the terminal energy acceptor and primary electron donor are shown to be able to accept or donate electrons when illuminated. And intact membranes, containing the entire photosynthetic machinery embedded within a lipid bi-layer are also shown to remain functional on a gold electrode, turning electrons over for days, under constant illumination and at ambient conditions.

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Controlling Photosynthetic Antenna Assembly and Functioning via Cofactor Exchange

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LH1 antenna and the reaction center form the photosynthetic unit of purple photosynthetic bacteria, the simplest biological nanodevice which with very high efficiency captures photons and converts their energy into chemical energy. To gain control over the assembly and functioning of this antenna, we have developed methods to manipulate pigment composition of LH1 complexes by incorporation of modified bacteriochlorophyll or modified carotenoids. The insertion of Ni-substituted BChla as the ultrafast excitation trap in LH1 provided new information about the antenna functioning, inaccessible by other means. The analysis of LH1 emission quenching by the trap showed that LH1 unit comprises 20±1 BChl molecules and that a single trap per LH1 entirely quenches its emission. Femtosecond pump-probe experiments showed a 60 fs deactivation channel in the Ni-BChla-substituted LH1, which originates from a one-exciton state delocalized over the entire LH1 ring of about 20 BChla molecules.

The carotenoids strongly promote LH1 formation from its subunits. The promoting effect is enhanced when carotenoid contains the hydroxy or methoxy side groups, implying that in parallel to hydrophobic interactions and π-π stacking other interactions, such as H-bonding, are also involved in the formation and stabilization of LH1. Carotenoids markedly affect ΔH° and ΔS° associated with LH1 formation in detergent but the driving force of the process remains almost constant due to efficient enthalpy-entropy compensation in the system. Following the carotenoid exchange approach a series of LH1 complexes with different carotenoids was obtained, in which the mechanism of Crt-to-BChl energy transfer could be investigated.

Our studies show that LH1 is a versatile model system whose assembly and photophysical properties can be easily controlled via cofactor exchange. These features make the LH1 complex a very promising model system for the design of bio-inspired deviced performing solar energy conversion.

Hybrid Quantum Dot-Metal Nanoparticle Systems: Connecting the Dots

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Transmission of information between qubits for quantum communication and computing will require directed nanoscale transmission that maintains the quantum character of the information. One paradigm proposes to achieve directed nanoscale transfer by coupling qubits, for example, in semiconductor quantum dots (SQD) to plasmonic nanoantennas made from metallic nanoparticles (MNP). Such hybrid nanoscale structures could transport excitations as well as coherent states. At the same time, intriguing reports suggest that coherent excitation transport plays a role in photosynthesis. To address these possibilities, we study theoretically the response of model hybrid nanostructure molecules consisting of SQDs coupled to MNPs subject to applied optical fields.

Quantum coherent time evolution of the SQDs in the hybrid molecule is found by solving the SQD density matrix equations. This system has been studied for a single SQD interacting with a spherical MNP in the weak [1], and strong coupling regimes [2, 3]. In strongly driven, strongly dipole-coupled SQD-MNP hybrids with spherical MNPs, interference, phase-shifts at resonance and self interaction define the MNP/SQD coupling and lead to Fano resonances, exciton induced transparency, suppressed SQD response and bistability [1–3]. More complicated response can be tailored by using MNP shape and the placement of SQDs to control the local near-fields that couple the MNPs and SQDs [4]. We identify regimes where coupling to MNP dark modes and higher order multipolar modes dramatically changes interference and self-interaction effects. Excitation transfer is studied by considering systems of interacting SQDs, both when the SQDs interact directly without an MNP and when the interaction is mediated by an MNP. The physics of the MNP/SQD coupling and the excitation transfer will be elucidated. Consequences for engineering a quantum bus between SQD qubits using plasmonics will be elaborated.

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Atomistic Theory of Exciton Fine Structure Splitting in Self–Assembled Quantum Dots

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Continuous matter approaches like effective mass approximation or kp method proved to be capable of describing main features in electronic and optical spectrum of quantum dots [1,2]. Yet these methods are limited by the fact that the resolution on the scale of a unit cell is lost. Proper description of true atomistic symmetry is of paramount importance if both qualitative and quantitative predictions are to be made. One of the most striking examples concerns the bright exciton splitting [3], which is observed even for fully shape-symmetric dots [4], where the straightforward k*p theory predicts no splitting in this case [5]. Undoubtedly the theory including atomistic details that accounts for lattice symmetry, material interfaces and substrate orientation is crucial for understanding optical spectra of quantum dots including excitonic properties.

The fine structure splitting (FSS) of excitonic emission in self-assembled quantum dots (QDs) originates from the electron-hole exchange interaction. In the effective mass approach, FSS occurs due to the lateral shape anisotropy of the QD's confining potential, vanishes for cylindrical QDs, and increases proportionally to the axial deformation [4,5]. Using atomistic sp3d5s* tight-binding approach combined with configuration interaction method (CI) [6,7], we compute electron-hole exchange matrix elements. The long ranged electron-hole exchange interaction, and hence the FSS, is decomposed into the contribution due to the zinc-blende lattice anisotropy, which is present even in nominally cylindrical dots, and a contribution due to the QD shape anisotropy. Further, for systems deformed away from the cylindrical symmetry we demonstrate that because of the underlying crystal lattice, FSS depends on the choice of the deformation axis in a non-trivial way.

These atomistic calculations allow for the detailed understanding of the FSS in realistic quantum dot structures. Tailoring of InAs/InP QDs emission properties by growth on InP nanotemplates [8] should result in a reduction of FSS, an important step toward efficient quantum dot based entangled photon pair sources.

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Scanning Gate Microscopy Simulations for Quantum Rings

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The scanning gate microscopy [1] (SGM) is a technique that allows for mapping the conductance (G) of a mesoscopic semiconductor system in function of the position of the scanning microscope tip floating above the structure. The charged tip interacts electrostatically with the two-dimensional electron gas and thus probes the electron flow several nanometers below the surface. The conductance maps gathered for the two-dimensional electron gas in the vicinity of the quantum point contact [2] resolved the spatial electron wave functions at the Fermi level including the interference fringes due to elastic scattering. The scanning gate technique was used [3,4] for observation of the deflection of the electron trajectories by the Lorentz force acting on the Fermi level electrons. Classical scarred orbits of open quantum dots (quantum billiards) were resolved, [5,6] and flow of current through quantum rings [7-10] were also studied.

We simulated [11] the electron flow through a quantum ring [7] in presence of the external charge of the tip. For that purpose we solved the DFT equations for the "electron gas" formed by up to several hundred electrons within the computational box. We determines the actual potential introduced by the charged tip and calculated the conductance using the Landauer approach. We found that the screening of the repulsive potential of the tip involves an appearance of the Friedel oscillation of the electron density. For the tip localized above the center of the channels the effective potential along the channel turns out to be Lorentzian of width that is comparable to the tip-electron-gas distance. This width is surprisingly insensitive to both the electron density and the charge localized at the tip.

We have studied the relation between the conductance maps and the local density of states at the Fermi level. We have found that the details of the latter can be deduced from the G maps only provided that the width of the effective potential of the tip is much shorter than the Fermi wavelength. To get a possibly close correspondence between these two functions it is therefore recommendable to study conductance of low density electron gas and approach the tip to the gas at a shortest possible distance. According to our results the extraction of LDS features by G mapping is only possible for a weakly perturbing potential of the tip. Otherwise, the tip modifies the electron density below the tip producing a wide range of possible G maps without any evident relation with the non-perturbed LDS. We found that large positive charges at the tip lead to formation of concentric conductance maps while the strong negative charges produce radial fringes within the ring and concentric ones outside the ring. We have demonstrated that the radial fringes within the ring appear for interrupted current circulation around the ring. They are insensitive to the external magnetic field. We argued that this results from the exclusion of the Aharonov-Bohm effects for the electron flow along a single path. We found that the concentric fringes that appear for the tip outside the ring depend on the external magnetic field and the dependence is due to an interplay of the electrostatic and the magnetic Aharonov-Bohm effects.

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Bright and dark plasmon excitations in metallic nanoantennas by single dipolar emitters

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Theoretical foundations for designing the radio-frequency antennas were established, and immediately followed by an experimental realization, over a hundred years ago. With a simple operating principle, half-wave dipole and Yagi-type antennas found applications in numerous bandwidths. More challenging have been attempts to apply analogous concepts to construct antennas for the visible part of the electromagnetic spectrum [1]. It has been recently shown that gold nanorods [2] hold promise as tunable visible light antennas [3].

In our work, we consider a response of plasmonic gold nanorods in a system comprising a single nanorod and an emitting dipole positioned either along the nanostructure's major axis, near its tip or beside it, near its middle. Such geometries are suitable for generating „dark plasmons", in contrast to a plane wave excited single nanorod, where „bright plasmon resonances" can be efficiently generated. As „dark plasmons" do not exhibit radiation losses, they could be used for more efficient waveguiding in periodic structures. Furthermore, exploration of the mechanism of dark plasmon excitation is essential for understanding the modification of emission from molecules in vicinity to metallic structures [4].

The results were obtained by numerical simulations carried out using the BEM (Boundary Element Method) approach [5] and compared to a simple optical antenna model [6]. In the first geometry we investigated, the dipole was placed near the tip of nanorod. It has been shown [7] that this structure is an inefficient pathway of exciting dark plasmon modes, regardless of chosen polarization. As a measure of this process, we use both radiative and non-radiative decay rates of the dipole, with the first one being an indicator of the mode's „brightness", and the latter – of the dipole-nanorod coupling. The behavior changes substantially when a lowered-symmetry system is considered, with the dipole positioned near the middle of nanorod. Due to an inhomogenity of the electric field, a very efficient excitation of both quadrupole dark and multipole bright modes is possible. Furthermore, we have observed a high selectivity of the radiative nature of plasmon modes due to the polarization of the dipole.

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Self-Assembly of Nanoscale Colloids

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Self-organization of nanoparticles and nanoscale objects in general represents one of the most dynamic areas of modern science. Better understanding of these phenomena is important from both fundamental and practical perspectives because nanoparticle self-organization processes
(1) identify similarities between biological and non-biological nanoscale species;
(2) lead to unusual optical properties from different combinations of nano- and microscale features;
(3) can potentially simplify manufacturing of electronic, photonic, and sensing devices.

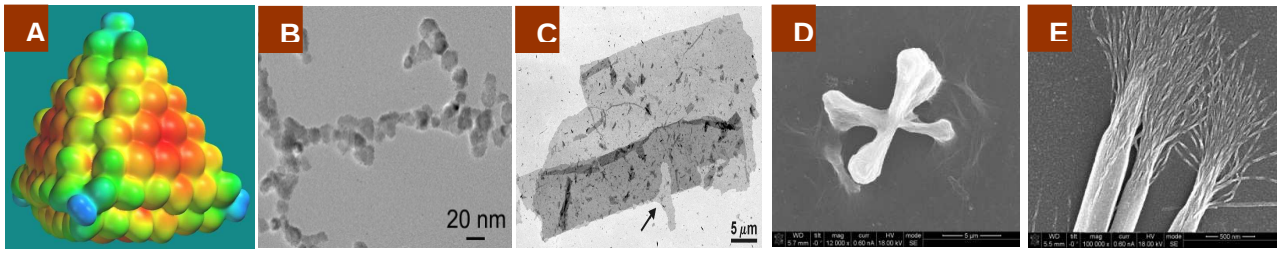

Figure 1: (A) Atomic model of CdTe NPs used in quantum mechanical calculations. (B) Self-assembled chains of ZnO NPs. (C) Self-assembled NP sheets from CdTe NPs. (D) Transient "dog-bone" 3D assemblies of CdTe NPs. (E) Twisted nanoribbons.

Over a period of last decade we demonstrated that intricate 1D, 2D, and 3D systems from CdTe, CdS, Au, ZnO nanoparticles could be formed. It was achieved by exercising fine degree of control over attractive and repulsive interactions between nanoparticles. Pivotal roles in expanding the variety of self-assembled structures were attributed to factors determining anisotropy of the force fields around nanoparticles: geometry of the nanoparticle facets, crystal lattice, dipole moments, distribution of a stabilizer, and intrinsic chirality of the nanoparticle cores. Rationalization of the topology of the self-assembled structures (Figure 1) in the framework of different contributions to the force fields, such as electrostatic, dipolar, hydrophobic forces, and hydrogen bonding will be presented. Fine tuning of the interactions also resulted in finding dynamic nanoparticle assemblies capable of restructuring in response to different media parameters.

The analysis of the self-assembly processes for nanoparticles also revealed surprising analogies with self-organization behavior of biological macromolecules. Besides examples mentioned above, a case of self-assembly of inorganic analogs of viral capsids was also demonstrated. The idea of nanoparticle-protein analogy was also extended to other protein functions. Latest data on the design of inorganic biomimetic inhibitors, enzymes, and cellular signaling agents based on inorganic particles will be presented. Advantages and limitations of protein replications by nanocrystals will be discussed.

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Nanoscale Metrology – Key Process in Application of Nanoobjects

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Nanoobjects demonstrate exceptional properties that make them suitable for new and exciting possibilities in the area of nanotechnology. Applications of nanoparticles due to their unique properties include improved wear resistance, new anti-corrosion properties, the potential for the design and development of complex structures, drug delivery and early detection, antiviral and antibacterial agents, and many others.

Metrology of nanometer-sized objects requires the development of new testing procedures, the use of unconventional methods or devices and focus on the phenomena negligible or absent in the macroscale.

The presentation will demonstrate the results of synthesis and characterization of metallic nanoparticles. Particular attention will be directed to the physico-chemical characterization. Dynamic Light Scattering, Atomic Force Microscopy, Scanning/Transmission Electron Microscopy results of monodisperse gold and silver nanoparticles will be shown. Important parameters of nano-objects, whose knowledge is essential in their applications will be discussed.

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Hybrid Nanostructure Composed of Light-Harvesting Complexes and Au Nanoparticles

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Photosynthesis is one of the most important biochemical conversions occurring on the earth. Thorough knowledge of the various processes and mechanisms controlling this transformation will give us the opportunity for more efficient utilization of solar energy in photovoltaic processes or in the process of artificial photosynthesis. To achieve this goal, we have conjugated light-harvesting complexes that participate in photosynthesis with inorganic nanoparticles which improve the optical properties of the latter [1-4].

Our research is focused on the peripheral antenna photosynthetic complex peridinin-chlorophyll-protein (PCP) isolated from Amphidinium carterae. This complex is water-soluble and has relatively simple structures which make it suitable for our study. A PCP's monomer contains two chlorophyll a and eight peridinin molecules. All pigments are embedded in a protein matrix. Absorption spectrum of PCP features broad and intense bands between 400 nm and 550 nm that match plasmon resonance of gold nanoparticles present at 520 nm.

We can distinguish four main methods to conjugate biomolecules on gold nanoparticles surface: direct ligand exchange, the use of a biofunctional linker, surface coating and electrostatic adsorption. In our work we conjugated the light-harvesting complex with gold nanoparticles using straptavidin-biotin interaction. The streptavidin-biotin bond is perhaps one of the strongest non-covalently interacting pair; the binding is relatively fast and only slightly affected by the pH, temperature, solvents, etc.

To allow the chemical functionalization of photosynthetic complex a two mutations of PCP were obtained with Cys incorporated to the protein to which biotin was next attached. On the other hand in order to link a streptavidin to gold nanoparticles, the EDC cross-linking procedure was applied [5]. The efficiency of our functionalization and conjugation procedure was measured directly by investigating plasmon-induced fluorescence quenching due to the interaction between PCP and metallic nanoparticles. Through establishing the appropriate conditions, we expect to obtain the enhancement of fluorescence of the photosynthetic complexes.

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Edge States and Flat Bands in Graphene Nanoribbons with Arbitrary Geometries

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Graphene nanoribbons (GNR), stripes of nanometric widths cut from graphene, are the subject of a growing interest. They exhibit edge-localized states, which may play an important role in transport and magnetic properties. For instance, the magnetic properties of nanoribbons are directly related to the existence of localized edge states [1]. All these edge terminations have been experimentally identified by different techniques, such as scanning tunneling microscopy [2,3], high-resolution transmission electron microscopy [4], or atom-by-atom spectroscopy [5]. It is thus important to identify general edges and nanoribbons that present localized edge states, as well as their degeneracy and characteristics.

We prescribe general rules to predict the existence of edge states and zero-energy flat bands in graphene nanoribbons and graphene edges of arbitrary shape [6]. No calculations are needed. For the so-called minimal edges, the projection of the edge translation vector into the zigzag direction of graphene uniquely determines the edge bands. By adding nodes to minimal edges, arbitrary modified edges can be obtained; their corresponding edge bands can be found by applying hybridization rules of the extra states with those belonging to the original edge. Our prescription correctly predicts the localization and degeneracy of the zero-energy bands at one of the graphene sublattices, confirmed by tight-binding and first-principles calculations. It also allows us to qualitatively predict the existence of E = 0 bands appearing in the energy gap of certain edges and nanoribbons.

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Collective Luminescence from Arrays and Ensembles of Quantum Dots

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The emission of light from systems composed of two quantum dots (QDs) and from larger ensembles of QDs is affected by the collective interaction of the QDs with the modes of the electromagnetic field and by the coupling between the dots. In the case of a double-dot structure, these two factors may result in non-exponential decay of the exciton population and coherent luminescence, which is reflected in the linear and non-linear optical response of these systems. Collective effects can also lead to population trapping in dark states and to non-monotonic temperature dependence of the exciton life time, similar to that observed experimentally. In the case of dense ensembles of QDs, the collective character of the spontaneous emission in the presence of inter-dot coupling leads to an enhanced emission rate, as indeed found in a recent experiment. Our results indicate that long-range (dipole) interactions via the common electromagnetic reservoir are not sufficiently strong to account for the experimentally observed effect. However, additional short-range interactions (which may arise due to tunnel coupling) can indeed lead to faster radiative decay, in quantitative agreement with the experimental findings.

Metallic and Semiconductor Colloidal Nanocrystals with Specific Functionalities

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The synthesis of colloidal nanocrystals, functionalized with organic ligands, is discussed. The focus will be on materials either synthesized by the hot-injection method or just by a simple heating up approach. Both approaches are suitable to obtain materials with specific functionalities and can provide nanocrystalswith high monodispersity. The latter are suitable for self-assembly of them into ordered superlattices. In addition, the functionality of the as synthesizednanocrystals can be tuned by making use of cation exchange reactions, after synthesis. Examples are shown where this tool is used to increase photoluminescence efficiencies, to shrink or widen band gap energies, to increase magnetic coercivity, or to dope semiconductors by magnetic ions.

Triangular Silver Nanoparticles: Their Preparation, Functionalization and Properties

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The field of plasmonics is a rapidly growing area of research and holds much promise for the improvement of diagnosticsand photonics.Our group has recently developed a highly reproducible and rapid seed-mediated method to prepare triangular silver nanoplates.[1] These particles have well defined surface plasmon resonance (SPR) bands which can be tuned throughout the visible and near IR and therefore show great promise for MEF and SERRS applications.[2] They exhibit high sensitivity to changes in the medium refractive index, which depends markedly on the aspect ratio of the nanoplates .[3,4]

Silver nanoparticles are more challengingto functionalise than the analogous gold system, as they are prone to oxidation andare susceptible to degradation by chloride ions. A number of different approaches for stabilising the nanoplates and for their functionalization with small DNA molecules (oligonucleotide ODNs) will be discussed.

The preparation of hollow triangular AuAg nanoboxes, [5] their subsequent functionalisation with small DNA molecules (ODNs) (AuAg-ODN) and the formation of assemblies by hybridisation of complementary AuAg–ODN conjugates will be reported.Nanoassemblies may also be formed by combining spherical gold nanoparticle ODN conjugates(Au-ODN) with complementary AuAg-ODN conjugates (Figure 1).

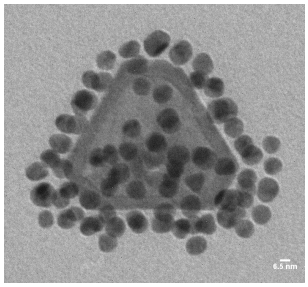

Figure1: Assembly of complementary Au-ODN and AuAg-ODN conjugates

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Submicrometer Silica Particles with Plasmonic Shells

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Noble metal nanostructures exhibit surface plasmon resonances at certain wavelengths, which depend on particle shape, size and surrounding medium. At resonance they may accumulate energy of electromagnetic field in regions near their surface called “hotspots”. This energy buildup can produce a dramatic enhancement of optical responses of matter in vicinity of plasmonic structures. This allows applications such as surface enhanced Raman spectroscopy (SERS), fluorescence enhancement, optical absorption enhanced in photovoltaic devices just to mention a few. Plasmonic resonances of metal nanoparticles have finite width, hence control of resonance position through for example dimensions is crucial. Nanoshells made of dielectric core and metallic shell are an example of structures with great tunability [1]. Random, semicontinuous, metal films (SMFs) are a type of plasmonic structures with broad absorption. SMFs are metal-dielectric layers made of random, fractal type [2] nanometer-sized metallic structures such as clusters and elongated islands that resonate in a broad spectral range, extending from the UV into the near-IR and beyond [3]. These films are usually made on planar substrates using vacuum evaporation, but it is also possible to synthesize them for instance on spherical particles.

We report fabrication and optical properties of submicrometer silica particles with plasmonic gold shells. In fabrication process we used commercial silica microspheres and synthesized silica rods. Both types of silica structures were functionalized with amino groups. Gold shells of desired morphology were fabricated by reduction of gold salt on the surface of functionalized silica. Optical properties of fabricated core-shell structures with different cores and shell types were characterized in aqueous solution. The spectra reveal strong dependence of extinction of core-shells on plasmonic shell nanostructure.

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Optical Spectroscopy on Nanostructured Spin-Hybrids

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Combining electrical, magnetic and optical functionality in one single device is regarded as an engineer's dream. Two approaches might be suitable for achieving this ambitious goal: Semiconductors can be doped with magnetic ions and, alternatively, metallic ferromagnets might be combined with semiconductors in a hybrid approach. Here, we present an overview on our recent research on spin-hybrids based on semiconductors.

In a first series of experiments, nanostructured ferromagnets are combined with magnetic semiconductors in order to obtain local spin control via the fringe field. Microstructured Fe/Tb multilayer ferromagnets with out-of-plane magnetization were used to imprint a remanent magnetization into the magnetic ion system of the underlying semiconductor. This results in a locally varying carrier spin polarization of up to 25 % at zero external fields [1]. We demonstrate the ability of switching the magneto-optical response of the semiconductor by reversing the magnetic state of the ferromagnet via an intense laser pulse [2]. Replacing the ferromagnet by a miniaturized coil providing magnetic field pulses in the GHz regime, we are able to show that the semiconductor magnetization can be switched even electrically on a sub-ns time scale.

In a second series of experiments, we investigate magnetically doped nanocrystals, where the optical and magnetic functionality are combined within a single material system. Exciting Mn2+ - doped CdSe nanocrystals with a picosecond laser pulse is shown to result in a photoinduced magnetic ordering of the manganse spins. Very large effective internal magnetic fields are observed that lead to a complete magnetization of the nanocrystals in the absence of an external magnetic field. Signatures of photomagnetization are observable even at room temperature [3]. We extend the experiments to Mn2+-doped CdSe nanoribbons. A pronounced magneto-optical response is observed for both, heavy hole and light hole exciton transitions all the way up to room temperature as a result of the strong quantum confinement. These large spin effects could lead the way to a new generation of spin-based semiconductor devices combining high temperature operation and cost-efficient assembly from colloidal precursors.

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Spectroscopy of Semiconductor Quantum Dots with Single Magnetic Ions

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The ability to detect and manipulate a single spin in semiconductor low-dimensional structures has recently attracted a lot of interest. Particularly, CdTe quantum dots with a single isoelectronic Mn2+ impurity seems to be a very promising candidate for the building block of future information storage and processing devices. Recent experiments have shown the possibilities to read and manipulate the electronic spin state of the Mn2+ ion in such dots. This not only enables the use of such system as a memory device, but also allows investigation of interactions of an isolated magnetic ion with crystal lattice or carriers trapped in the quantum dot. Moreover, a presence of a single magnetic ion in a quantum dot gives the possibility to observe certain features of excitonic states which are not readily observable in nonmagnetic dots. For example dark exciton states are usually inaccessible for optical spectroscopy. However, the mixing of dark and bright states, induced by the magnetic impurity, can make the observation dark excitons possible.

The talk summarizes recent results of the studies of the spin dynamics and the information storage on the single Mn2+ ion in a CdTe quantum dots performed both in low and high magnetic fields. Possible mechanisms of the orientation and relaxation of the Mn2+ spin will be discussed, including the role of the dark exciton recombination in the spin orientation process. Moreover, a measurement of the spin-lattice relaxation time will be presented, showing an example of exploitation of the the unique possibility to optically access the single Mn2+ ion spin state.

Novel Approach for Energy Spectrum Probing in Nanostructures

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A new technique, electron counting spectroscopy has been used to probe the electronic properties of semiconducting CdSe quantum dots [1]. This technique allows us to fill or empty a semiconducting quantum dot with many electrons. The ability to shift the Fermi energy by a large amount holds promise for nanoscale or molecular electronics, since the large energy separation between the levels often has limited access to only few levels.

The detection scheme is based on an original approach where the investigated particle is attached to only one electrode, a carbon nanotube. The conductance of the nanotube is measured as a function of a gate voltage (V_g), which allows the detection of individual electrons transferred onto the quantum dot. The electron transfer occurs only when the electrochemical potential of the nanotube matches the energy levels in the particle, while sweeping the gate voltage. We noticed no electron transfer for certain range of V_g which is attributed to the energy gap of the CdSe quantum dot. Our study shows that single-electron detection with CNT transistor represents a new strategy to study the separation in energy between the electronic discrete levels of the semiconducting quantum dot. In particular, it allows the study of the chaotic behavior of the electronic levels in the CdSe particle [1].

Additionally, we discuss the possibility of applying electron counting spectroscopy to investigate other type of quantum dots, e.g. gold nanoparticles.

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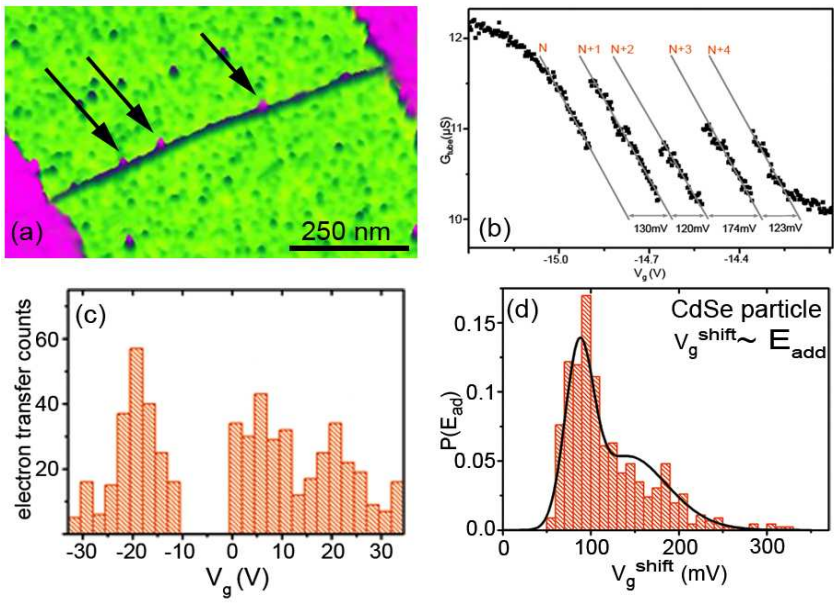

Fluorescence Mapping of PCP Light-Harvesting Complexes Coupled to Silver Nanowires

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Localized electromagnetic field enhancement generated through the plasmon oscillations in metalic nanoparticles affects both absorption and emission of nearby placed dipoles and strongly depends on system spatial arrangement [1]. Therefore a precise tuning of the geometry of metallic nanoparticles should provide a way to improve absorption efficiency of the sunlight energy in natural light-harvesting complexes. Peridinin-chlorophyll-protein (PCP) is a relatively simple light-harvesting antenna with well known structure [2] and spectral properties [3]. Those features make PCP a great model system for investigating plasmon-induced changes of optical properties in this biomolecule. Recent reports have shown that fluorescence intensity of PCP can be significantly increased by coupling to a silver island film [4].

In this work we employ fluorescence confocal microscopy to study the optical properties of PCP complex coupled to a single silver nanowire. The length of the nanowire was about 10 µm with diameter of 200 nm. Relatively big sizes enable us to image the position of the nanowires and compare their placement with PCP fluorescence intensity map. Separation between the PCP complexes and nanowires was achieved using a SiO2 spacer layer with various thickness. Depending on the distance between nanowire and protein we have observed changes in the PCP fluorescence intensity characterized with a maximum for the spacer thickness of 10 nm. Furthermore we have observed that emission is much stronger for PCP placed near the ends, rather than the middle of nanowire. We conclude that electromagnetic field is more strongly localized at the ends of the nanowires.

Financial support from the WELCOME program "Hybrid nanostructures as a stepping-stone towards efficient artificial photosynthesis" awarded by the Foundation for Polish Science is acknowledged.

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Nanoparticles Affect the Function of Photosystem I

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Plasmonic metal-nanostructures are an emerging tool for manipulating optical properties of fluorophores. They are used for enhancing the sensitivity of fluorescence-based assays in drug discovery and high-throughput screenings as well as in immunoassays. Even plasmon-assisted detection of biological reactions in vivo has been suggested. The fast evolving range of applications for plasmonic nanomaterials make a deeper understanding of nanostructure–protein interactions necessary.

The effect of plasmonic interaction on the properties of proteins is investigated by single-molecule techniques. During the last years it turned out that photosystem I – a key complex in photosynthesis – can serve as a model complex for multi-chromophore FRET-coupled systems (1). The investigated nanostructures are formed by gold and silver. Beside remarkable fluorescence-enhancement significant changes of the characteristic fluorescence emission from photosystem I were observed. Particularly the higher energy chlorophylls with site-energies close to the reaction center show increased deactivation via fluorescence emission, thereby, reducing the efficiency of energy transfer towards the site of charge separation (P700), and thereby, the protein function. This reduction will also affect the efficiency of PSI-nanoparticle hybrids discussed for biotechnological applications (2). It can be supposed that altered responses can generally be expected for multi-chromophore FRET-coupled systems near to plasmonic nanostructures. The observed spectral changes are discussed in a general framework of plasmonic interaction with multi-chromophore FRET-systems (3).

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Modulation of Intraprotein Electron Transfer Rate in Bacterial Reaction Centers

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Photosynthetic bacterial reaction centers are in many aspects the best model systems for studying intraprotein electron transfer. They are very stable, it is easy to mutate them, the electron transfer may be triggered by ultrashort laser pulses, and the electron transfer reactions occur on very different time scales from picoseconds to seconds. In this short talk, as an example, back electron transfer from the reduced primary electron acceptor to the oxidized primary donor will be presented. This reaction occurs on nanosecond time scale and its rate is modulated by a number of factors: internal electric field in the protein, temperature and free energy gap between the charge separated states. Mechanism of this modulation will be explained.

Spectral Dependence of Fluorescence Enhancement in LH2-Au Nanoparticle Hybrids

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Sun is almost endless source of energy and nature have made use of it in efficient way by the process of photosynthesis. It would be highly attractive to mimic and perhaps make better light harvesting devices to collect as much as possible of sunlight energy. One of the routes is goes through constructing hybrid devices composed of natural photosynthetic pigment - protein complexes that would surpass performance of natural systems. The efficiency of light harvesting of natural photosynthetic complexes can be achieved by coupling the natural complexes with metallic or semiconducting nanoparticles [1,2].

In this work we study the optical properties of hybrid nanostructures composed of LH2 membrane antenna complexes from purple bacteria (*Rps. palustris*) and gold spherical. We attempt to optimize the effect of plasmon induced fluorescence enhancement by varying the separation between the two constituents, and spectral distance between plasmon and excitation.

Peripheral antenna complex LH2 shows major absorption bands in the near-infrared and are due to strongly coupled bacteriochlorophylls arranged in two rings, B800 and B850. The complex features also carotenoid absorption between 430 nm and 560 nm. The samples were prepared by spin-coating gold nanoparticles on glass substrate. Then SiO_2 layer was evaporated with thickness from 4 nm to 40 nm. Finally, we spin-coated LH2 embedded in a PVA polymer solution on top of SiO_2 layer. We study the structure composed of LH2 complexes coupled with 5 nm gold spherical nanoparticles with plasmon resonance at 530 nm. Fluorescence measurements show that for a 12 nm thickness spacer and 485 nm excitation wavelength the intensity is five times higher (see Fig. 1) than for a reference sample (d = 40 nm). But for 405 nm excitation wavelength intensity is only twofold higher for 12 nm thickness spacer than for reference sample. For shorter distances fluorescence quenching is dominant in both cases. Importantly, fluorescence decay time show no dependence upon the spacer thickness.

Enhancement is dependent on excitation laser wavelength. Results show that for bigger spectra distances from plasmon there is less interaction between LH2 and gold nanoparticles. These results indicate that by careful design of hybrid nanostructures it is possible to optimize plasmon induced effects on complex biomolecules and thus enhance their functionality - in this case – light harvesting. Planned single molecule experiments will clear up processes responsible for the observed effects.

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Photonic Structures for Fluorescence Enhancement of Pigment-Protein-Complexes: A Single Molecule Study

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In recent years the ever increasing availability of structurally well-defined nanoparticles has led to a growing interest in the interaction between plasmonic nanostructures and single chromophores. Evidence for fluorescence enhancement of dye molecules as well as multichromophoric systems by noble metal nanoparticles has been detailed in the literature [1-3].

Here we present an extensive study comprising more than 13.000 individual Light Harvesting 2 complexes (LH2) from *Rhodobacter sphaeroides* interacting with gold nanoparticles (AuNPs) of well defined shape and size.

The fluorescence intensities of single LH2 in close proximity to single AuNP are clearly enhanced. Our findings are consistent with a simple theoretical model.

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Protein Maquettes – Tools to Study Electron Transfer

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Protein maquettes, known also as *de novo* designed or artificial proteins, are very powerful tools for *in vitro* study of natural electron transfer processes. The protein maquettes have well defined, robust structure, and a few strictly defined properties, securing e.g. specific ligand binding. The maquettes which bind porphyrines (heme and chlorophyll derivatives), iron-sulfur clusters and also the maquettes which coordinate both types of cofactors will be presented. The protein scaffold of all discussed maquettes is the bundle of four amphiphilic helices. The porphyrine binding is possible due to introduction of histydyl residues on opposite helices, inside hydrophobic core of bundle, while iron-sulfur cluster coordination depends on the presence of four cysteinyl residues. Four types of iron-sulfur cluster binding place were studied: (i) coordination within one loop with four cysteinyl residues (ferredoxin-like type), (ii) symmetric, with two loops, each of two cysteines (Fx site of photosystem I), (iii) with double symmetry, each cysteine coming from independent, spatially distant loop (L-subunit of light-independent protochlorophyllide oxidoreductase) and (iv) with cysteinyl residues located on helix, inside hydrophobic core (artificial fold). Designed proteins are easily overexpressed in bacterial systems (mostly *E.coli*), purified and reconstituted with cofactors. The design strategy, as well as characterization of final protein product will be described.

The maquettes presented here may be directly used as a tool to study electron transfer, which is the basis of life-crucial processes, photosynthesis and mitochondrial oxidation. But, due to its properties, these proteins may be also used in future nano-bio-devices construction, e.g. in biosensors.

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Corroles Versus Porphyrins on the Basis of Their Spectral and Photophysical Properties

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The new era began for corroles when the first practical methods of triarylcorroles synthesis were reported in 1999. Those tetrapyrrolic compounds belong to the porphyrinoid family, whose best known members are porphyrins. The electronic absorption and emission spectra of the metalled corroles are similar to those of the analogous porphyrins. They present several visible Q bands and usual single and intense B (Soret) band in the near-UV region. Both bands of corroles are more solvent-sensitive and are redshifted compared to porphyrins. Moreover the corrole Q bands are stronger and the Soret bands weaker than the corresponding porphyrins. The metallation and deprotonation cause the fluorescence quantum yield increase in the corroles, in contrast to porphyrins. That can be explained in part by ring distortion (from domed to very planar macrocyclic structure), very large structural rigidity which is reducing the probability for non-radiative relaxation (IC) and not supporting intersystem crossing of the singlet excited state to the triplet (ISC) (a light metal i.e. Φ_f of 0.76 for Al(tpfc)$(py)_2$). The S_1 fluorescence lifetimes are in the nanosecond time scale. The fluorescence quantum yields from the second excited singlet states of metallocorroles are very weak ($\sim 10^{-4}$) and the main relaxation path to the S_1 state is the internal conversion with a sub-picoseconds time scale. Moreover there is no evidence that dark states participate significantly in the electronic relaxation process of those corroles, in contrast to porphyrins [1].

Corroles have many interesting spectroscopic and photophysical properties like dual S_2-S_0 and S_1-S_0 fluorescence, high quantum yields of S_1-S_0 fluorescence, high quantum yields of singlet molecular oxygen in oxygenated solutions and facile synthetic access to water soluble derivatives. This fact suggests that they would be attractive alternatives to the porphyrins used in dye-sensitized photovoltaic cells and photodynamic therapy and proposed for use in photon-actuated molecular logic devices.

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Metal-Enhanced Fluorescence of Corrole Molecules

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Corroles are synthetic, aromatic macrocycles of tetrapyrrolic family that also includes porphyrins, phthalocyanine sans vitamin B12. These dyes were synthesized in 1965 [1], but the interest in these compounds has grown recently as these molecules could be used for antitumor therapy, catalytic and optical sensor devices [2], and artificial light-harvesting systems. It is well known that plasmon-fluorophore interaction can lead to substantial changes in fluorescence intensity [3]. One of the critical parameters influencing this interaction is the distance between the dye and the metallic nanoparticle.

In this work we study fluorescence properties of corroles deposited on single silver nanowires, which were coated with a dielectric layer of silica with thickness ranging from 5 to 30 nm. The silica layer was deposited on spin-coated nanowires using e-beam vacuum deposition technique. Next, a layer of 5,10,15-tris(pentafluorophenyl)corrole molecules in PMMA matrix was spin-casted. We chose the silver nanowires for two main reasons – firstly, the plasmon resonance of this metallic nanoparticles is located around 400 nm, exactly where the main peak of corrole absorption appears, secondly, the length of the nanowire is about 10 µm, thus allowing us to optically locate the nanowires on the substrate. In this way we can correlate the position of the nanowire with the emission pattern observed for the corroles.

To image the sample we use a confocal scanning fluorescence microscope. First, using reflection of the 532 nm laser light we locate the nanowires, and subsequently, we scan the same region and detect the corrole fluorescence. In the case of thick spacers (30 nm) we observe weak, twofold fluorescence enhancement. In contrast, for thin (5 nm) spacers the enhancement of the corrole fluorescence reaches factor of 15. As expected, the enhancement factor strongly depends on the thickness of the dielectric spacer. Moreover, our experimental setup allows for spatially resolved measurement of both fluorescence spectra and fluorescence lifetimes from any given location on the map. In this way a complete information regarding the interactions present in our system can be obtained. The results demonstrate that the interaction between plasmon resonance induced in a single silver nanowire can enhance the fluorescence of corrole molecules, and by proper design of the substrate we are able to control this influence.

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Measuring the Electronic Properties of Single Semiconductor Nanowire Heterostructures Using Advanced Optical Spectroscopies

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There has been intense interest in recent years to control the electronic structure in quasi one-dimensional nanowires through the fabrication of novel axial and radial heterostructures. Unlike materials in higher dimensions, nanowires have the unique ability to grow axial or radial heterostructures between almost any two materials regardless of lattice mismatch or strain. Understanding exactly how the electronic properties of the nanowire are changed through this control is extremely important and requires spectroscopies with high spatial, temporal and spectral resolution. I will discuss a number of examples in which the electronic structure in nanowire heterostructures can be modified, and what insights can be provided by a number of single nanowire optical spectroscopies such as Raman, photoluminescence (PL) and photoluminescence excitation (PLE).

I will particularly discuss the very recent development of a new experimental technique, photomodulated Rayleigh scattering spectroscopy which provides a new way to measure ground and excited electronic states even in cases where photoluminescence spectroscopy is not possible. The Rayleigh scattering from semiconductor nanowires is strongly polarization sensitive which allows a nearly background-free method for detecting only the light which is scattered from a single nanowire. While the Rayleigh scattering efficiency from a semiconductor nanowire depends on the dielectric contrast, it is relatively featureless as a function of energy. However, if the nanowire is photomodulated using a second pump laser beam the internal electronic structure can be resolved with extremely high signal to noise and spectral resolution. The photomodulated Rayleigh scattering spectra can be understood theoretically as a first derivative of the scattering efficiency which results from a modulation of the band gap and depends sensitively on the nanowire diameter. Most importantly, this new technique can be easily extended so as to measure dynamics within a single nanowire in a pump-probe configuration

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Interfacing Quantum Dots with Atomic Vapors

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Single quantum dots are efficient single photon sources and possess all the advantages of solid state systems: scalability, tunability, optical as well as electrical excitation as well as their inconvenients: inhomogeneous broadening and short dephasing times. Using a new type of quantum dots made of GaAs in an AlGaAs matrix, we have generated single photons at the frequency of the D_2 transition in Rb, fine tuning of the dot emission was performed by applying a magnetic field on the quantum dots. The propagation of the single photon stream in the rubidium vapour results in slow light where single photons travel at c/15. This interface between a single quantum dot and an atomic vapour enables additional experiments, such as quantum memories.

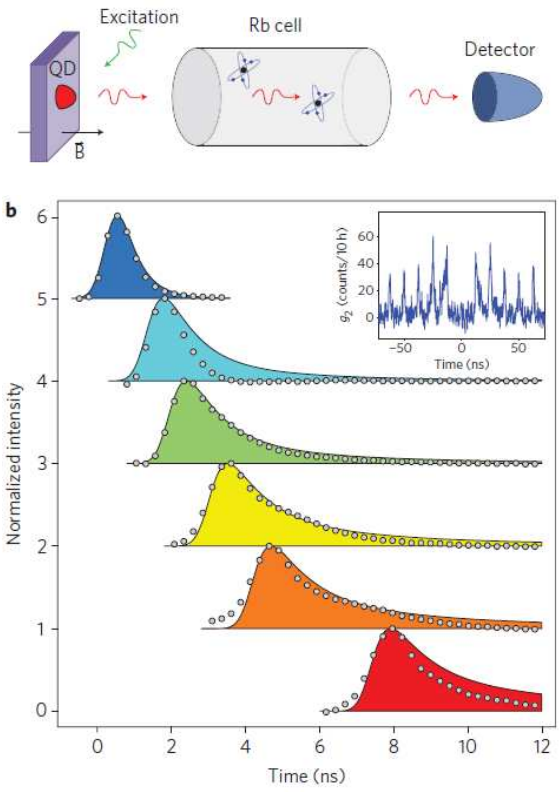

Fig. 1. (top) Schematics of the experiment. The emission from a single quantum dot is coupled to a warm rubidium cell. (bottom) slow light measurements, with increasing rubidium density, the time delay increases reaching velocities as slow as c/15. The inset show a photon correlation measurement.

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Self-Assembled Free-Standing Semiconductor Nanowires: Doping, Stability and Core-Shell Structures

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Free-standing nanowires have attracted a lot of scientific interest recently [1], an interest which is due to the promising applications of these wires in devices and the fact that they can now be reproducably realized experimentally using the vapour-liquid-solid (VLS) method. With these nanowires several nanostructures are already fabricated, such as FETs, p-n diodes, bipolar junction transistors and also sensors for chemical and biological substances. Continued progress towards integrated nanoelectronic circuits will require advances in our ability to better control the electronic properties of these building blocks and to assemble them into increasingly complex structures. Considerable efforts have been placed on doping e.g. Si and Ge nanowires to control their electrical properties. However, doping of nanostructures remains a challenge as a result of both fundamental synthetic issues and statistical fluctuations that are intrinsic to homogeneous doping of small structures. Moreover, charged dopant centers will limit the mobility and the corresponding performance of these semiconductor nanowires. In thispresentation we focus on the structural, electronic and phonon properties of such self-assembled free-standing nanowires and study the effect of doping and covering the wire with a shell.

An *ab initio* study of the formation and segregation energies of B and Pdoped and BP codoped silicon and germanium nanowires oriented along the [110] direction is performed for fully relaxed H-passivated wires with a diameter of 1.2 and 1.6 nm [2]. We found that the B and P dopants will migrateto the edge of the wire and that the formation energy for codoping is smaller than that for the single doped cases.In ultrathin wires it is possible to have a larger number of dangling bonds than dopant atoms per unit length; theeffect of these defects on the formation and segregation energy is substantial. We found that P dopants are more easier trapped, and thus become electronically inactive, than B dopants.

Knowledge of the behavior of phonons in a material can be important for several applications, as the thermalproperties of semi-conducting systems, such as the thermal conductance, are governed by phonons and their dispersionand interactions. Therefore we studied the phonons [3]in the same passivated silicon nanowires by performing full *ab initio* calculations of the phonon dispersion, byutilising density-functional perturbation theory (DFPT). We used these calculated phonon spectra to determine thestability of the nanowires. The occurence of imaginary frequencies indicates structural instabilities. These can be caused by computational limitations, e.g. the small size of the unit cell typically used in *ab initio* calculations.

Full *ab initio* techniques are applied to study the electronic and dynamical properties of free standing, hydrogen-passivated Si/Ge core-shell nanowires oriented along the 110 direction [4]. All studied wires exhibit adirect band gap and are found to be structurally stable. The different contributions of the core and shell atomsto the phonon spectra are identified. The acoustic phonon velocities and the frequencies of some typical opticalmodes are compared with those of pure Si and Ge nanowires. These depend either on the concentration or on the

type of core material. Optical modes are hardened and longitudinal acoustic velocities are softened withdecreasing wire diameter.

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Electronic Transport through Bilayer Graphene Flakes

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Graphene is one of the most studied materials nowadays due to both to its exotic fundamental properties and its prospecticve application in future nanoelectronics. To this purpose, one- and zero-dimensional structures such as graphene nanoribbons and flakes are of great relevance.

In this talk I will present the electronic properties of bilayer graphene flakes. These systems can be built by overlapping two semi-infinite ribbons or depositing a monolayer flake onto a graphene ribbon. These two possibilities are of a complementary nature as to their transport properties, which are analyzed by employing a continuum Dirac model and a tight binding approach. We have found several periodicities in the electronic conductance, related to the energy, system size and interlayer coupling, which can be further modulated by applying an external voltage bias. The transport properties show marked oscillations between zero and the maximum value of the conductance. These caracteristics can be applicable for the design of electromechanical switches.

Controlling the State of a Single Magnetic Atom with Electric Current

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A scanning tunneling microscope (STM) can probe the inelastic spin excitations of a single magnetic atom in a surface via spin-flip assisted tunneling in which transport electrons exchange spin and energy with the atomic spin [1-5]. If the current induced excitation rate is larger than the atom relaxation rate, the STM current can drive the spin out of equilibrium. Here we show theoretically how the spin orientation of a single magnetic adatom can be controlled by spin polarized current. Spin polarized transport electrons produce a torque on the spin, driving it away of equilibrium. We have modeled the inelastic tunneling using an effective spin Hamiltonian that accounts for spin-flip assisted tunneling experiments, including a single Mn atom [2], a Mn dimer [2,4] and Fe-Phthalocyanine molecules [6]. This phenomenological spin model is further supported by a microscopic cotunneling theory [7]. Using rate equations we are able to successfully describe the non-equilibrium spin dynamics of the magnetic atoms, which, for a non-polarized tip, results in non-monotonic dI/dV curve. In the case of spin polarized STM, the spin orientation of the magnetic atom can be controlled parallel or anti-parallel to the magnetic moment of the tip, in agreement with recent experiments [4]. We show that by changing the direction of the applied voltage, the orientation of the magnetic adatom can be completely reversed on a time scale that ranges from a few nanoseconds to microseconds, depending on bias and temperature. The changes in the adatom magnetization direction are, in turn, reflected in the tunnelling conductance. Therefore, this effect opens the possibility of writing/reading a single spin without the need of a local magnetic field.

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POSTERS

Influence of Plasmon Resonance in Silver Island Film on the Optical Properties of Light-Harvesting Complex PCP

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Plasmon excitation in silver island film (SIF) has been recently applied to efficiently enhance the optical properties of organic dyes [1], semiconductor nanocrystals [2], and light-harvesting complexes [3]. As a continuation of previous work, we focus on varying the morphology of the SIF surface and studying its impact on the optical properties of a peripheral photosynthetic complex peridinine-chrolophyll-protein (PCP) isolated from the algae *Amphidinium carterae*. The SIF layer was obtained by chemical synthesis based on reduction of $AgNO_3$ using NaOH and D-glucose. By controlling reaction time of SIF synthesis we are able to change the silver island density on a glass substrate: from an ensemble of very isolated islands to quasi-continuous metllic film. Obtained metallic substrates were analyzed using atomic force microscopy and absorption spectroscopy to determine plasmon resonance frequency. The maximum of plasmon resonance changes from 390 nm to 450 nm, depending on the reaction conditions. On such prepared substrates we deposit thin PVA polymer layer containing PCP complexes.

The impact of the plasmon resonances in the SIF layer on the optical properties of the PCP complexes was investigated by means of fluorescence emission and excitation spectroscopy, and time-correlated single photon counting technique with the excitation at either 405 nm and 485 nm. While the emission of the PCP complexes on glass substrate features monoexponential decays with characteristic times around 3.7 ns, the PCP complexes deposited on the SIF are characterized by a bi-exponential decay. In addition, fluorescence maps, measured by scanning confocal microscopy, showed us that the PCP complexes on SIF surface exhibit ehanced fluorescence emission in comparison with the reference sample.

The results show that by varying the morphology of the SIF substrates we can control the optical properties of the light-harvesting biomolecules.

Support from the WELCOME program “Hybrid nanostructures as a stepping-stone towards efficient artificial photosynthesis” awarded by the Foundation for Polish Science is acknowledged.

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Protochlorophyllide Oxidoreductase in Prolamellar Bodies – the Unique Enzyme in Unique Membranes

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Chlorophylls belong to the most important molecules in the whole world of biochemical compounds. In Angiosperms, the key step in chlorophyll biosynthesis is the reduction of protochlorophyllide (Pchlide) to chlorophyllide (Chlide). This reaction is triggered by light and catalysed by a very unique enzyme - a light dependent protochlorophyllide oxidoreductase (LPOR, EC 1.3.1.33), in the presence of NADPH. In etiolated seedlings, the Pchlide photoreduction occurs in pre-chloroplast form of plastids (etioplasts) in a paracrystalline lipid structure named prolamellar body (PLB) and induces changes in the PLB structure, that precedes the etioplast-to-chloroplast transformation.
We induced alterations in the PLB structure in darkness by incubation with chaotropic salts (i. e. KI), detergents and by pH changes, and monitored changes in fluorescence properties of Pchlide. To go deeper into the understanding of the molecular mechanism of Pchlide-enzyme interaction, *in vitro* experiments were performed using the *A. thaliana* LPOR overexpressed in *E. coli*. Furthermore, the homology model of *A. thaliana* LPORA was made to obtain a representation of its tertiary structure, which has not been modeled up to now. The sequence analysis was done to recognize ligand binding sites and catalytic motifs. Other bioinformatic tools were applied to compare LPOR and the light-independent Pchlide oxidoreductase (DPOR). These two enzymes are generally regarded as evolutionary unrelated, but surprisingly, a similar sequence fragment was found in LPOR and one of the light-independent Pchlide oxidoreductase subunit. The biological role of this motif, named TFT due to its three first amino acids, is discussed.

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Charge Separation in Photosystem I - Studied by Using Ultrafast Optical Spectroscopy

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Photosystem I (PSI) is a large pigment-protein complex embeded in thylakoid membrane. It utilizes the light energy to drive the transmembrane electron transfer. The central part of PSI, called the reaction center (RC), contains two branches of electron transfer cofactors (A and B) and is surrounded by the antenna system containing ~90 chlorophyll *a* molecules. The antenna system harvests the light and delivers its energy to the RC, where the electron transfer is initiated. Chlorophyll dimer P700 located at the common end of two branches is considered in the classical view to be a primary electron donor. However, the exact mechanism of the charge separation process in PSI is still matter of debate.

In order to test the recent models of charge separation in PSI and check whether the electron transfer is initiated in one or both electron transfer branches, we performed a series of ultrafast transient absorption and fluorescence experiments for PSI from green algae *Chlamydomonas reinhardtii*. The results of our experiments suggest that (1) in algal PSI both branches of electron transfer cofactors are equally engaged in electron transfer, (2) the primary charge separation is a reversible process, (3) the primary electron donor is rather the accessory chlorophyll A and not P700 as it was generally accepted before.

Our studies of charge separation in PSI are perfect example showing how development of new experimental techniques and strategies leads to the overthrow of paradigms existing in the description of photosynthetic processes and how big research effort is still needed to fully describe these phenomena. The precise understanding of the mechanisms of natural photosynthesis seems to be a necessary step towards the creation of the efficient artificial photosynthesis.

The Silver Colloidal Solutions and Silver Films for Efficient SERS

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The silver colloids and silver films are known for their enhancing properties in Raman spectroscopy. Here we present a study on the preparation of silver colloidal solution and deposition of silver films on mica. The colloidal solutions were examined by two methods: the UV-VIS spectroscopy to determine their optical properties and atomic force microscopy to determine the size of the particles and structure of the deposited films. The crystal violet aqueous solution was used as a test sample for evaluation of enhancing properties of silver colloidal solutions and films. These test experiments showed that both colloidal solutions and films deposited on mica are efficient SERS substrates, therefore they can be used in further studies for enhancement of the Raman signal of biopolymers, for instance polysaccharides and DNA.

Plasmonic Interaction of Highly Ordered Metal Nanostructures and Pigment Proteins

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Controlling the interaction of nano particles and biological systems is an ongoing challenge in nanotechnology. Hybrids between molecules and nano particles are used in catalysis, or nano particles penetrating cell systems function as diagnostics (fluorescence enhancement, MRT or ESR active). In our study we use Photosystem I (PSI) of oxygenic photosynthesis as a model system for multi-chromphore FRET-coupled systems to study interactions with highly ordered plasmonic metal nano structures created by shadow nanoshpere lithography [1].

PSI is an efficient light harvesting complex composed of 96 chlorophylls leading the excitation energy to the reaction center to induce electron transfer over the membrane. At low temperatures excitation energy can be trapped on some energetically low lying chlorophylls (red chlorophylls), leading to a significant fluorescence quantum yield. In recent experiments we reported remarkable differences in the wavelength position and the spectral diffusion properties of these red chlorophyll states [2].

In this study we investigate the influence of plasmonic metal nano structures on PSI complexes deposited on nano structured surfaces.

The intensity of the fluorescence emission of the individual complexes is remarkably enhanced. In addition to the enhancement we observed changes in the width and center position of the emission spectra, which is indicative for changes in the composition of the contributing emitters. A modification of the fluorescence lifetime and the FRET-coupling of chlorophyll molecules participating in the energy transfer process by coupling to plasmonic modes of the metal nano structures can explain the observed changes[3].

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Fabrication and Optical Properties of Rod-like Silica Core/Semicontinous Gold Shell Microstructures

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Metal-dielectric nanostructures have a great potential for various applications due to their unique optical properties. These materials exhibit surface plasmon resonance at certain wavelengths and accumulate energy of electromagnetic field in nanosize regions called hot spots. The spectral position of resonances is dependent on geometry of nanostructures and types of materials they are made of. One of the most studied metal-dielectric nanostructures are spherical submicron structures made of dielectric core and metallic shell or vice versa. This type of geometry is called core-shell. Currently metal-dielectric core-shell structures are investigated for many applications including surfaced enhanced spectroscopies such as Raman spectroscopy (SERS) [1,2], IR spectroscopy (SEIRA) [1,2] or fluorescence spectroscopy (SEF) [3], and cancer therapy [4],

Mentioned above spherical metal-dielectric nanostructures are only one type of possible geometries. The great number of potential applications is also associated with possibility of fabrication of metal-dielectric structures with various geometries including planar structures such as semicontinuous metal films (SMFs) or core-shell particles of various shapes.

We report here results of investigations on fabrication and optical properties of micrometer size (diameter 100-300 nm, length 800-1200 nm) silica rods covered with semicontinuous gold shell of few tens nanometers thickness. Silica rods were fabricated according to method developed by Kujik et al. [6] and functionalized with amine groups. The metallic shell was formed by reduction of gold salts on amine-functionalized silica rods. The examples of SEM images of fabricated silica rods and rod-like silica-gold core-shell structures are shown on Fig 1. The modification of silica core synthesis and shell fabrication conditions allowed us to obtain structures with different geometry of core and shell.

Initial studies have shown that optical properties of fabricated structures are strongly dependent on morphology of metallic shell.

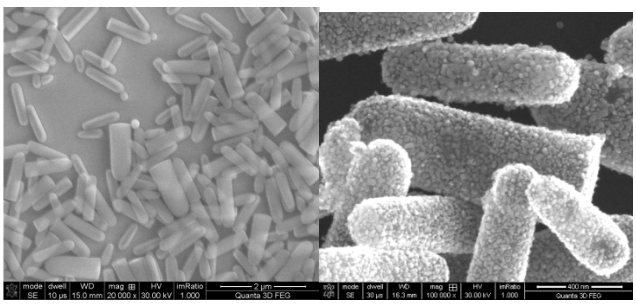

Fig. 1. SEM images of rods structures; on left – SiO_2 rods, on right - functionalized SiO_2 rods covered with gold layer – core-shell structures

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Dynamics of Protein Elements of Hybrid Structures - Molecular Dynamics Simulations of Light Harvesting Protein Model

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Hybrid nanostructures are often composed of inorganic parts and “biological” ones. Highly optimized through million years of evolution light harvesting proteins are hard to mimic synthetically, thus crucial elements from these systems are attached in experimental hybrid structures that should have improved charge separation properties [1]. Among the most promising proteins is peridinin-chlorophyll-protein from Amphidinium carterae (PCP) [2]. It has a wide absorption spectrum (420-550 nm), optimized for sunlight. The structure of this protein has been solved [2]. The charge transfer properties of a similar system has been quantum-mechanically studied [3] but the dynamics of this protein, used in modern nanotechnology, has been not addressed yet. The proteins dynamics is important from the theoretical point of view, since any calculations of the energy transfer process should take into account a natural flexibility and possible orientation changes of the chromophores. The role of mutations on spectra may be easily studied. Quite often so called functionally important motions also facilitate the protein function. The dynamical change of the electrical field in locations of the chromophores affects their photophysics as well.

In this work we will present our preliminary results of PCP modeling using a well established molecular dynamics (MD) methodology. The CHARMM27 force field parameters were prepared for this protein and for basic chromophore components. The system was embedded in a box of water, with proper counterions, MD simulations were run using the NAMD code [4]. The current trajectory statistics is rather poor, this is ongoing project, and in the poster we will discuss several practical related to MD simulation of similar hybrid nanostructures.

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Characterization of Porphyrin-TiO2 Complex Using EPR and Raman Spectroscopy

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Hybrid complexes consisting of porphyrin derivatives conjugated with metallic or semiconductor nanostructures show better photodynamic activity than that of the original photosentizer. On the basis of *in vitro* studies these complexes have been suggested suitable for photodynamic therapy of cancer [1, 2, 3].

Meso-tetrakis (4-sulphonatophenyl) porphyrin (TSPP) and its complex with TiO_2 were studied by electron paramagnetic resonance (EPR) and Raman spectroscopy. A TiO_2-TSPP complex was obtained by covalent bonding of anionic porphyrin with nanostructural form of TiO_2. In a previous work we have reported deactivation processes of this complex, a photosensitization mechanism has also been proposed [4].

Measurements by Raman spectroscopy and EPR are necessary to obtain information about the interaction between TSPP and TiO_2 and radical formation, respectively. The EPR signals of the samples were recorded in dark and under illumination. In Raman spectra the active modes of the symmetry A_{1g}, B_{1g} and E_g associated with TiO_2 were observed, whereas for TSPP-TiO_2 complex very strong luminescence in the spectral range related to the dye and the absence of bands associated with TSPP were detected.

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Fluorescence of Protochlorophyllide in Model Systems and in Prolamellar Body

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Protochlorophyllide (Pchlide), a natural porphyrin-type compound, is one of the intermediates of the chlorophyll biosynthesis pathway. In dark-grown angiosperm seedlings, Pchlide accumulates in etioplast inner membranes, mainly within a prolamellar body (PLB), which is a regular paracrystalline lipid structure. Besides Pchlide, also its esterified form – protochlorophyll (Pchl) has been detected in etioplasts, however, it amounted to only a small percentage of the total accumulated porphyrins.

To understand Pchlide interaction with its molecular surroundings in PLB, which is essential to follow the process of PLB formation, a multi-approach investigation of Pchlide in isolated PLB and in model systems has been performed. The analysis of fluorescence properties of Pchlide and Pchl in different model systems, i.e. organic solvents, micelles and liposomes was the focus of the presented study, both for monomeric pigments and in the course of their aggregation. The specific pigment-solvent interactions were observed in protic solvents (alcohols) and in histidine. Using different fluorescence quenchers, localization of Pchlide molecule with respect to lipid chains of liposomes was proposed. Next, Pchlide-LPOR complexes, which naturally occur in PLB, were reconstituted using the A. thaliana LPOR overexpressed in E. coli and examined with fluorescence methods. On the other side, fluorescence studies were performed for isolated PLBs treated with different factors, (chaotropic salts, detergents, temperature, pH changes).

Up-converted Fluorescence Microscopy of $NaYF_4$ Nanocrystals Doped with Er^{3+}/Yb^{3+} Ions

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We report on microscopy imaging of up-converted fluorescence in $NaYF_4$ nanocrystals doped with Er^{3+}/Yb^{3+} ions with concentrations about 2% and 20% respectively. The nanocrystals were synthesized following the procedure developed by Boyer et al. [1]. Observed size distribution of the nanocrystals was quite homogenous with average diameter about 20-30 nm [2]. Several samples with varying concentration of the nanocrystals were prepared, starting from the stock solution (60 mg/ml) down to 0.3 μg/ml. Samples were dispersed in 2% polymethyl-methacrylate (PMMA), then spin-coated on the microscope glass slides and systematically examined using confocal fluorescence microscope. The excitation was 980 nm whereas detection was set at green up-converted emission from erbium (540 nm). For highly concentrated samples measured fluorescence maps are quite homogeneous, however for lower concentrations we observe well-resolved circular spots, which we attribute to emission from individual nanocrystals.

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Strong Quantum Memory at Resonant Fermi Edges: Shot Noise Evidence

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The Fermi-edge singularity, which originates from the Coulomb interaction of conduction electrons with those on a localized discrete level (core shell electrons or QD levels), was first predicted in the x-ray spectra of metals [1,2] and constitutes a paradigmatic exactly solvable many-body problem [3]. Signatures of the Fermi-edge singularity are observed also in resonant tunneling set-ups, where the necessary transient scattering potential due to changes of the charge occupation of the discrete level is induced by tunneling events. The dynamical response of electrons in, say, the emitter lead results in enhanced tunneling probability whose characteristic feature is the power law dependence on the electron energy with a (truncated) singularity at the emitter Fermi energy [4,5].

The proper description of the transport set-up is done by an extension of the original Fermi-edge singularity model, where no charge transfer between the continuum and the localized level(s) is considered, to the interacting resonant level model. As shown in recent experiments [6], noise in this regime displays characteristic behaviour (including a super-Poissonian maximum) which cannot be accounted for by the Markovian theory.

Since the Fermi-edge singularity transport set-up involves both many-body correlations and quantum coherence it is reasonable to expect large non-Markovian corrections in the singularity region. We show that this is indeed the case and that including the non- Markovian effects accounts for all of the qualitative features of the noise, as well as allows for viable quantitative predictions.

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Sol-gel Titania Composite Coatings Containing ZrO_2 Nanoparticles

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Recently, fine inorganic nanoparticles have come under discussion, with distinct suggestions that they can improve the mechanical properties of the material. There are two possible ways to improve the tribological properties of the material with the use of nanoparticles. The first one is to embed nanosized particles in the material, which are responsible for a substantial increase of the fracture toughness, hardness and wear resistance of the material, whereas the second one is to create nano-sized structures or patterns on the surface which reduce the contact area between two surfaces and therefore can be used for reducing adhesion and friction.

The aim of this study was to create patterns on the titania surface, as unevenly distributed agglomerates consisted of ZrO_2 nanoparticles, to improve the tribological properties of the material.

Titania coatings and titania composite coatings with patterns were fabricated using sol-gel, spin-coating method on silicon wafers Si (100). Friction and wear experiments were conducted on patterned and non-patterned titania surfaces using a Tribometer T-23 under a dry-sliding condition with normal load 80 mN.

Atomic force microscopy measurements revealed that the structure of this coatings are different. Pure titania coatings are smooth, whereas the composite coatings have agglomerates like structures on the surface with the height up to 1 μm. Consequently, the mechanical behaviour of these systems were expected to be different. It has been found that the patterned titania surface with ZrO_2 agglomerates showed a reduction in the coefficient of friction up to 45% as compared with the non-patterned surface. Wear experiments also showed that the presence of surface textures on the titania coatings resulted in lower scars width, with minimal material transfer to the sliding surface.

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AFM Investigation of Biological Nanostructures

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Nanostructures created by living organisms, optimized through millions of years of evolution, can be a valuable inspiration for nanotechnology. Atomic force microscopy (AFM) is an ideally suited tool for investigation of those objects, both because of its superb resolution and the ability to measure mechanical properties. Our poster presentation will cover AFM imaging and force spectroscopy of nanostructures that are part of caddisfly silk and diatomic frustules. Additionally, we aim to show the abilities of commercial and custom made AFM equipment found in Department of Biophysics and Medical Physics and encourage collaboration in research of hybrid and biological nanostructures.

Caddisfly larvae are well known for their ability to spin silk, which serves as an adhesive tape to glue various materials and catch prey in aqueous environment. AFM imaging of caddisfly silk, performed for the first time by our team, have shown that its surface is patterned with 150 nm humps. This pattern can be a feature vital for caddisfly silk exceptional underwater sticking abilities. Results of force spectroscopy of protein structures found on the surface will also be presented.

A characteristic feature of diatoms is that they are encased within a unique silica cell wall called frustule. It has a highly patterned surface, which gives an advantage of significant mechanical resilience. Additionally, frustule is covered with striae, which are small holes allowing cellular interaction with the environment. Our poster will cover AFM imaging of frustules as well as results of adhesion measurements inside of striae. Since striae are in fact 500 nm sized valves, its investigation can lead to development of new selective filters.

Excitation Dynamics in Photosystem I – Comparative Studies of Isolated Complexes and Whole Cells

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Naturally occurring photosynthesis is the most widespread on our planet process of converting solar energy into chemical energy. In cyanobacteria, algae and higher plants the light-dependent phase of photosynthesis is carried out by two types of pigment-protein complexes: photosystem I (PSI) and photosystem II (PSII). Most of the pigments in PSI and PSII form antennas that capture sunlight energy and transfer it to reaction centers where charge separation occurs. Both photosystems are also equipped with additional light harvesting complexes which support effective collection of the light: LHCI connected to PSI and LHC II, which can be connect to both PS I and PS II.

The main purpose of this project is to compare the excitation dynamics in isolated PSI complexes with excitation dynamics in photosystem I working in the natural environment and under physiological conditions, i.e. in a whole living cell. To carry out this comparative analysis we planned a series of time-resolved fluorescence measurements for three types of samples prepared from the *Chlamydomonas reinhardtii* (green algae) cells: (1) isolated PSI core complexes, (2) isolated PSI-LHCI complexes, (3) whole cells with genetically removed photosystem II and reduced amount of LHCI and LHCII. So far we have performed time-resolved experiments for isolated core complexes and test measurements for pre-frozen whole cells. The poster will present the obtained data and results of their analysis.

The Study of DLS and UV-Vis Resolution in Case of Polydisperse Colloids

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Metal nanoparticles possess unique optical, electrical and mechanical properties which are strongly dependent on the size and the shape of the particles. These properties make possible to use nanoparticles in a wide range of applications e.g.: biomedical, electronics, optics, optoelectronics. Necessary condition for the use of nanoparticles is to understand their physical and chemical properties, in particular particle size.

One of the most popular methods of determining the size of nanoparticles is Dynamic Light Scattering (DLS), operating on the basis of laser light scattering measurements. This method is widely used by specialists in different scientific fields because measurement does not require any special sample preparation for analysis. Another advantage of the technique is short time in obtaining the result. DLS is an excellent analytical method for monodisperse colloids metrology. In the case of polydisperse colloids there is a risk that during the DLS measurement small objects maybe screened by bigger one. The subject of this study is to examine the sensitivity/resolution of the DLS and UV-Vis spectroscopy in the characterization of colloids with particles of different sizes.

In this presentation DLS, UV-Vis, Atomic Force Microscopy and Transmission/Scanning Electron Microscopy characterization of the monodisperse silver nanoparticles colloids will be shown. The colloids were intentionally mixed in appropriate ratios by volume. Then the prepared mixtures were studied using the DLS and UV-Vis techniques. Main aim of the study was to determine the threshold of objects detection in the polydisperse colloids.

Synthesis and Functionalization of Silver Nanowires

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Developing ways to control the morphology of metallic nanoparticles is extremely important for designing systems with well defined properties such as plasmon resonance frequency. One of many examples could be synthesis of gold nanorods that feature plasmon frequencies in the infrared spectral range, while spherical gold nanoparticles are confined to visible region only. Our goal is to assembly a hybrid nanostructure composed of metallic nanoparticles and light-harvesting complexes for efficient absorption of the sunlight [1].

In this work we synthesize silver nanowires with diameters from 60 to 150 nm and lenghts up to tens of microns, giving the aspect ratio of the order of 1000. The synthesis has been carried out using polyol method, which allows for relatively gentle temperature and pressure conditions for the reaction. Silver nitrate(I) AgNO3 is reduced using ethylen glycol in the presence of polivinylopirolidon (PVP): metallic silver is obtained in this way. PVP forms a shell on the metallic surface, prohibiting thus aggregation of metallic nanoparticles and inducing anisotropic growth of the nanowires.

The morphology of silver nanowires was studied using scanningelectron microscopy and absorption spectroscopy. Typical result of the first method is displayed in Fig. 1: the nanowires are more than ten micron long and approximately 60 to 100 nm wide. The plasmon resonance is present around 400 nm, matching well the absorption spectrum of the light-harvesting complex from algae.

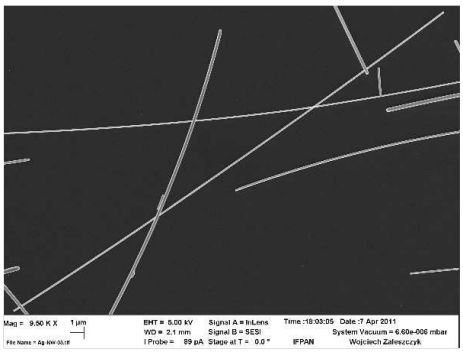

Fig. 1. SEM image of silver nanowires.

Future work will concentrate on functionalization of silver nanowires with thiol groups in order to facilitate conjugation with the photosynthetic complexes. The conjugated hybrid nanostructures will be characterized using optical spectroscopy techniques.

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