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International Workshop

On Hybrid Excitations in Nano-Materials

18|20 December 2011

Dept. Physics & CNR NANO S3 | Modena | Italy

# BOOK OF ABSTRACTS

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UNIVERSITÀ DEGLI STUDI  
DI MODENA E REGGIO EMILIA.



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**INTERNATIONAL WORKSHOP ON HYBRID EXCITATIONS IN NANO-  
MATERIALS**

**18-20 DECEMBER 2011**

**DEPARTMENT OF PHYSICS & CNR NANO S3– UNIVERSITÀ DI MODENA E  
REGGIO EMILIA | MODENA | ITALY**

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# PROGRAM

SUNDAY DECEMBER 18<sup>TH</sup>, 2011

## I SESSION

14:00 Opening (G. Goldoni, R. Di Felice)

14:30 **Amit Sitt**

*A core issue: The effects of core dimensionality in nano seeded rods on optical behavior and energy transfer*

15:15 Clementine Symonds

*Spatial coherence induced by plasmon/exciton strong coupling*

15:35 Tersilla Virgili

*Role of surface defects in the photophysics of a layer by layer assembled hybrid film*

15:55 Coffee Break

## II SESSION

16:25 Luca Bergamini

*Plasmonic properties of metallic nanoparticles coated by dielectric shells*

16:45 Carlo Andrea Rozzi

*Photo-induced charge-separation in light-harvesting supramolecular systems. A TDDFT perspective*

17:05 **Benedetta Mennucci**

*Surface enhanced fluorescence: an hybrid quantum mechanical/continuum model*

17:50 **Juan Ignacio Climente Plasencia**

*Excitons in semiconductor nanocrystals with polarized environment*

17:40 Discussion

20:30 Reception Dinner at Restaurant *Vecchia Pirri*, via Prampolini 8, Modena

## MONDAY DECEMBER 19<sup>TH</sup>, 2011

### I SESSION

- 09:00 **Ryan Artuso**  
*Hybrid quantum dot-metal nanoparticle systems: connecting the dots*
- 09:45 Fabio Della Sala  
*Electrostatic Field Driven Alignment of Organic Oligomers on ZnO Surfaces*
- 10:05 Arrigo Calzolari  
*Ab-initio study of hybrid interfaces for photovoltaic applications*
- 10:25 Coffee Break

### II SESSION

- 10:55 Sergio D'Addato  
*Metal and metal-oxide core-shell nanoparticles: A detailed study on assembling, structure and morphology*
- 11:15 Alessandro Mattoni  
*Large scale atomistic investigation of polymer-metaloxide hybrid interfaces*
- 11:35 **Natalia Del Fatti**  
*Optical response and ultrafast spectroscopy of metal-based hybrid nanoparticles*
- 12:20 **Garnett W Bryant**  
*Hybrid quantum dot-metal nanoparticle systems: connecting the dots*
- 13:05 Lunch at University Cafeteria

### III SESSION

- 14:30 **Liberato Manna**  
*Synthesis and assembly of complex nanocrystal structures*
- 15:15 Gabriele Rainò  
*Structural and Optical Properties of a Hybrid Nanocomposite Combining Dyes and Ag Nanoparticles in a Block Copolymer Micelle*
- 15:35 Claudio Fontanesi  
*Ag Nanoparticles (chemi)Adsorbed on Thiophene thin films grafted on Glassy Carbon*
- 15:55 Coffee Break & Poster Session

### IV SESSION

- 17:25 Markus Schuster  
*Manipulation of the distance between gold nanoparticles and a gold film by applied potentials*
- 17:45 **Yuriy Khalavka**  
*Synthesis of Linear and Hyperbrached Metal-Semiconductor Hybrid Nanoparticles*

18:30 Discussion

## TUESDAY DECEMBER 20<sup>TH</sup>, 2011

### I SESSION

- 09:00 **Ulrich Hohenester**  
*Simulation of a particle plasmons with the MNPBEM toolbox*
- 09:45 Sebastien Kawka  
*Energy transfer in weakly coupled hybrid nanostructures*
- 10:05 Simone Borlenghi  
*Spin transport and magnetization dynamics in heterogeneous nanostructures: A multiscale approach*
- 10:25 Coffee Break

### II SESSION

- 10:55 Valerio Voliani  
*Multifunctionalized gold nanoparticles for small intracellular delivery by non-linear excitations*
- 11:15 Malte Strozyk  
*One-sided growth of large Plasmonic gold domains on CdS quantum rods observed on the single particle level*
- 11:35 **Andrea Ferretti**  
*Hybrid functionals and gw corrections to quantum transport calculations*
- 12:30 Final Remarks

**Bold** font indicates invited speakers.

## POSTER SESSION

Localization of electron and hole gas in hexagonal core-multishell nanowires

Andrea Bertoni, Miquel Royo, Farah Mahawish, and Guido Goldoni

Designing all-graphene nano-junctions by edge functionalization: Optics and electronics

Caterina Cocchi, Deborah Prezzi, Alice Ruini, Marilia J. Caldas, and Elisa Molinari

Directional sensitization of ZnO nanorods by TiOPc supersonic beam deposition

Nicola Coppedè, D. Calestani, M. Villani, M. Nardi, L. Lazzerini, S. Iannotta, and A. Zappettini

Charge transfer dynamics in Ferrocene molecular architectures grafted on Si(111)

Claudio Fontanesi, D. Vanossi, F. Tassinari, F. Parenti, A. Mucci, L. Schenetti, and M. Innocenti

Electron scattering by interface phonons in a polar metal-oxide-semiconductor device

Anna Hauber and Stephen Fahy

Fully doped emeraldine oligomers: A theoretical study of the optical properties

Jasmina Petrova, Julia Romanova, Galia Madjarova, Anela Ivanova, and Alia Tadjer

Azobenzenes self assembled monolayers

Silvio Pipolo, Enrico Benassi, and Stefano Corni

Plasmon coupling effects between gold nanospheres and gold films

Alexander Schwemer, Markus Schuster, and Ulrich Rant

Valence band mixing of cubic GaN/AlN quantum dots

Carlos Segarra, J.I. Climente, and J. Planelles

## **ABSTRACTS OF TALKS**

# A CORE ISSUE: THE EFFECTS OF CORE DIMENSIONALITY IN NANO SEEDED RODS ON OPTICAL BEHAVIOR AND ENERGY TRANSFER

Amit Sitt, Shira Halivny, and Uri Banin

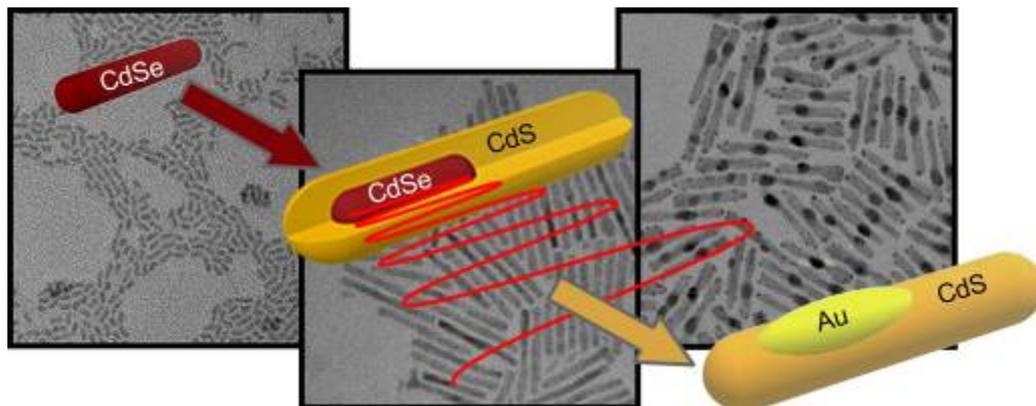
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Studying the transition of nanostructures as they develop from the zero-dimensional to the one-dimensional regime is significant for unveiling the modifications that occur in the electronic structure of the particle as its length to width aspect ratio is increased. Such understanding can lead to better design and control of the particle properties, making them attractive for a wide spectrum of technological applications. The ongoing improvements in the control of shape and morphology of nanoparticles in colloidal synthesis, which allows forming structures of similar composition but of different dimensionalities and shapes, open the way for probing such dimensionality effects.

Recently, a novel rod in rod system, in which a CdSe 1D rod acts as a seed for the growth of an elongated shell of CdS around it, was developed by our group.

In this talk, I will present several effects involving the 0D to 1D transition in CdSe/CdS core/shell nano heterostructures of different morphologies including “sphere in a sphere”, “sphere in a rod” and “rod in a rod”. Using these systems, I’ll demonstrate and discuss the changes which occur in the optical properties, and in particular in emission and absorption polarizations, as the dimensionality of the particles and of their cores changes. I’ll also discuss the use of these particles as donors in energy transfer processes, and show how the dimensionality changes of the particles’ core and shell can affect the donor’s time dependent survival probability, and may lead to systems with enhanced FRET efficiencies.



# SPATIAL COHERENCE INDUCED BY PLASMON/EXCITON STRONG COUPLING

S. Aberra Guebrou<sup>a</sup>, C. Symonds<sup>a</sup>, E. Homeyer<sup>a</sup>, J.C. Plenet<sup>a</sup>,  
Yu.N. Gartstein<sup>b</sup>, V.M. Agranovich<sup>b</sup>, and J. Bellessa<sup>a</sup>

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Strong coupling between disordered semiconductors and plasmonic or photonic modes has been evidenced in various materials like J-aggregated dyes [1], organic dyes [2] or layer of semiconductor nanocrystals [3]. These disordered active layers can be seen as a set of independent emitters randomly spread in a film. In this case, it has been shown theoretically that the polaritonic states are a mixing of one plasmon and a large number of excitations [4] and that the interaction with the photonic or plasmonic mode leads to the formation of an extended coherent state. The cooperative effects resulting from this coherence between a large number of otherwise independent emitters is investigated with optical experiments.

The system we studied consists of J-aggregated dye (TDBC) in interaction with a surface plasmon on silver. We investigate experimentally the spatial diffusion and coherence with a Young's interferences setup extracting luminescence emission from two different points of the sample [5]. The in-phase emission of regions separated by several microns is observed. These experiments are compared to a system in weak coupling regime where a different behavior is observed. The diffusion and interference experiments in strong coupling regime show that strong coupling leads to a macroscopic quantum state on several micrometers. This effect can be used for long range intermolecular energy transfers and can also offer an easy manipulation of this coherent state by structuring the metal or the organic semi-conductor.

[1] J. Bellessa, C. Bonnard, J.C. Plenet, and J. Mugnier, *Phys. Rev. Lett.* **93**, 036404 (2004).

[2] T.K. Hakala et al., *Phys. Rev. Lett.* **103**, 053602 (2009).

[3] D.E. Gomez, K.C. Vernon, P. Mulvaney, and T.J. Davis, *Nano Lett.* **10**, 274 (2010).

[4] V.M. Agranovich and Yu.N. Gartstein, *Phys. Rev. B* **75**, 075302 (2007).

[5] F. Dubin et al., *Nat. Phys.* **2**, 32 (2006).

## ROLE OF SURFACE DEFECTS IN THE PHOTOPHYSICS OF A LAYER BY LAYER ASSEMBLED HYBRID FILM

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We studied the optical properties of multilayered structures obtained by the alternation of CdSe nanoparticles and poly(p-styrenesulphonic acid) (PSSH) employing the layer-by-layer (LBL) technique, and compared the results with those obtained from diluted solutions of the same CdSe nanocrystals (NCs) capped with organic stabilizing molecules. These studies have put into evidence the important role of the environment surrounding the NC in the dynamics of photo-excited carriers, both when these stay stable in solution thanks to a capping layer and when they are assembled in the solid state in LBL thin films. In particular, we found that ultrafast pump-probe experiments performed on LBL films at high pump fluence reveal a rather broad photo-induced absorption (PIA) band overlapping with the photobleach at already 2 ps probe delay. Using microsecond to millisecond pump-probe experiments we inferred that the PIA band persists for several hundred  $\mu$ s. Moreover, we quantitatively analyzed the spectra at short and long time delays finding a clear evidence for a strong long-lived Stark effect. Remarkably, such a strong Stark effect was absent in the solution of capped NCs. Both observations give a clear indication of the presence of long-lived charged trap states in the LBL film. These traps are possibly related to the surface defects produced in the LBL process when capping molecules are substituted by the PSSH polymer. Finally, we also measured the photoluminescence spectrum at high pump fluence in both the solution of NCs and in the LBL film. Only in the latter we found the appearance of a weak band at shorter wavelength. The appearance of this auxiliary emission could be related to the existence of charged states in the LBL film.

# PLASMONIC PROPERTIES OF METALLIC NANOPARTICLES COATED BY DIELECTRIC SHELLS

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Dielectric shells surrounding a metal nanoparticle are known to modify the position and intensity of the plasmonic absorption band.

The existence of such coupling between the metal and the dielectric is well-established experimentally and represents the basis of detection systems such as LSPR (localized surface plasmon resonance) apparatus.

From the theoretical viewpoint, the optical properties of coated and uncoated metal nanoparticles are often interpreted in the framework of the long wavelength (i.e., non-retarded) approximation. The exact range of validity of this approximation and the magnitude of the related errors are not obvious. To shed light on that, we have studied the case of an uncoated and coated metallic sphere using formulas provided by both the general Mie theory and the non-retarded approximation. We have thus identified the breakdown of the non-retarded approximation as a function of particle size for various coated and non-coated metal particles.

In addition we have also modelled more complex system. We have focused on a metallic microsphere coated by two shells: the former is composed by azobenzene molecules and the latter, the external, by small gold nanoparticles. In this contribution we shall discuss the capability of the model to reproduce the experimentally determined behaviour of the compound, therefore identifying the microscopic origin of such behaviour.

# PHOTO-INDUCED CHARGE SEPARATION IN LIGHT-HARVESTING SUPRAMOLECULAR SYSTEMS. A TDDFT PERSPECTIVE

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Photo-induced charge separation is the kick-off condition for both photosynthesis and photovoltaic energy conversion. The photoexcitation step stores photon energy into the system, while the charge transfer step transforms the excitation energy into freely available electrochemical energy. By means of Time-Dependent Density Functional large-scale simulations we have investigated the femtosecond dynamics of photo-induced charge separation in a prototypical system, namely a supramolecular light-harvesting triad. The complex interplay of dynamical conformational adjustments and pure dipole-driven electron motion is such that a successful description of the phenomenon can only be obtained once the electron and nuclear dynamics are jointly considered and simultaneously solved. We identify relevant dynamical features of the process and indicate the crucial degrees of freedom governing its effectiveness.

# SURFACE ENHANCED FLUORESCENCE: AN HYBRID QUANTUM MECHANICAL/CONTINUUM MODEL

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An hybrid quantum mechanical (QM)/continuum model to predict surface enhanced fluorescence of molecular probes close to metal nanoparticles (MNP) will be presented and discussed [1,2]. The model can take into account the presence of a solvent and can treat arrays of MNPs of any shape [3,4]. In all cases, possible couplings among plasmon resonances in the arrays, and among plasmon resonances and solvent polarization in solvated MNPs, are taken into account in a self-consistent way.

Applications to realistic systems will be presented and used to explain and rationalize how intrinsic characteristics of the MNPs affects excitation processes and radiative/nonradiative decay channels of the probe.

Finally, the real QM nature of the nonradiative processes will be disclosed [5].

[1] S. Corni and J. Tomasi, *J Chem Phys* **118**, 6481 (2003).

[2] O. Andreussi, S. Corni, B. Mennucci, and J. Tomasi, *J Chem Phys* **121**, 10190 (2004).

[3] S. Vukovic, S. Corni, and B. Mennucci, *J. Phys. Chem. C* **113**, 121 (2009).

[4] A. Sanchez-Gonzalez, S. Corni, and B. Mennucci, *J. Phys. Chem. C* **115**, 5460 (2011).

[5] A. Munoz-Losa, S. Vukovic, S. Corni and B. Mennucci, *J. Phys. Chem. C* **113**, 16364 (2009).

# EXCITONS IN SEMICONDUCTOR NANOCRYSTALS WITH POLARIZED ENVIRONMENT

Juan I. Climente<sup>a</sup>, Jose L. Movilla<sup>a</sup>, Josep Planelles<sup>a</sup>, Miquel Royo<sup>a,b</sup>, and Guido Goldoni<sup>b,c</sup>

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We present a theoretical model to study the electronic properties of excitons in semiconductor nanocrystals interfaced with dielectrically mismatched environments. The model is based on the induced charge computation method [1], coupled to effective mass equations and configuration interaction routines [2-3].

First, we apply the method to study the influence of dielectric solvents on excitons confined in CdSe nanorods. We observe a large increase of the binding energy in agreement with related experiments [4], as well as a strong enhancement of the Coulomb correlations [5]. These effects become more noticeable in type-II CdTe/CdSe/CdTe nanostructures, where the wave function shape can be engineered through the environment [6].

Next, we apply the method to investigate the excitonic resonance in CdS-metal nano-hybrids. With reference to recent experimental reports, we specifically study CdS-based nanorods with metallic sectors deposited at the tips (matchstick) or metallic coatings (core-shell) [7]. In neutral matchstick structures the metal has only a minor influence (~1 meV) on the excitonic states. When the metallic sector is charged the exciton becomes rapidly redshifted and spatially indirect. In contrast, in neutral core-shell structures the exciton energy redshifts by tens of meV [8].

[1] D. Boda, D. Gillespie, W. Nonner, D. Henderson, and B. Eisenberg, *Phys. Rev. E* **69**, 046702 (2004).

[2] J.L. Movilla, J.I. Climente, and J. Planelles, *Comput. Phys. Commun.* **181**, 92 (2010).

[3] J.M. Badía, J.L. Movilla, J.I. Climente, M. Castillo, M. Marqués, R. Mayo, E.S. Quintana-Ortí, and J. Planelles, *Comput. Phys. Commun.* **182**, 533 (2011).

[4] D. Steiner, D. Katz, O. Millo, A. Aharoni, S. Kan, T. Mokari, and U. Banin, *Nano Lett.* **4**, 1073 (2004).

[5] J.I. Climente, M. Royo, J.L. Movilla, and J. Planelles, *Phys. Rev. B* **79**, 161301(R) (2009).

[6] M. Royo, J.I. Climente, J.L. Movilla, and J. Planelles, *J. Phys.: Condens. Matter* **23**, 015301 (2011).

[7] A.E. Saunders, I. Popov, and U. Banin, *J. Phys. Chem. B* **110**, 25421 (2006).

[8] J.I. Climente, J.L. Movilla, G. Goldoni, and J. Planelles, *J. Phys. Chem. C* **115**, 15868 (2011).

# HYBRID QUANTUM DOT-METAL NANOPARTICLE SYSTEMS: CONNECTING THE DOTS

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Hybrid molecules formed by coupling semiconductor quantum dots (SQD) to metal nanoparticle (MNP) nanoantennas provide a new paradigm for directed nanoscale transfer of quantum information. To assess this possibility, we study theoretically the response of these hybrid molecules to applied optical fields. Quantum-coherent time-evolution of the SQDs in the hybrid molecule is found by solving the SQD density matrix equations. We study hybrid molecules in the weak and strong coupling regimes. In strongly driven, strongly dipole-coupled SQD-MNP hybrids with spherical MNPs, interference, dispersion near resonance and self interaction define the MNP/SQD coupling and lead to Fano resonances, exciton induced transparency, suppressed SQD response and bistability. 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. We describe how coupling to MNP dark modes and higher order multipolar modes impact interference and self-interaction effects. The physics of the MNP/SQD coupling is outlined.

# ELECTROSTATIC FIELD DRIVEN ALIGNMENT OF ORGANIC OLIGOMERS ON ZnO SURFACES

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ZnO surfaces are very important substrates in different fields such as catalysis, blue-laser and photovoltaics. We present a theoretical study on the physisorption process of various organic oligomers (sexiphenyl, PPV6, sexithiophene, ...) on the ZnO(1010) surface. We used dispersion-corrected first-principles density-functional theory, MP2 and a novel non-empirical embedding method, based on the fast-multipole method (FMM). We find that both in-plane location and orientation of the molecules are completely determined by the coupling of their multipolar moments to the periodic dipolar electric field present at the semiconductor surface, while exchange-correlation-dispersion effects are almost constant for any translation/rotation of the molecule in a plane parallel to the substrate. The adsorption is associated with the formation of a molecular dipole moment perpendicular to the surface, which bears an unexpected linear relation to the molecule-substrate interaction energy. Long oligomers such as sexiphenyl become well-aligned with stabilization energies of several 100 meV along rows of positive electric field, in full agreement with recent experiments. These findings define a new route towards the realization of highly-ordered self-assembled arrays of oligomers/polymers on ZnO(1010) and similar surfaces.

[1] F. Della Sala, S. Blumstengel, and F. Henneberger, *Phys. Rev. Lett.* **107**, 146401 (2011).

# AB INITIO STUDY OF HYBRID INTERFACES FOR PHOTOVOLTAIC APPLICATIONS

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Metal-oxide nanoparticles (especially TiO<sub>2</sub>, ZnO, SnO<sub>2</sub>) may be sensitized to harvest visible radiation in working solar cells, upon molecular dye functionalization. However, at present the principles regulating interactions between the oxide layer and the rest of the photovoltaic (PV) cell are poorly understood. Indeed, upon molecular sensitization, semiconductor surface interacts with molecules in a wide range of possible scenarios, driving the formation of hybrid interfaces with specific spatial arrangement and novel electronic properties, and affecting both the light harvesting and the generation of the photovoltaic current.

By means of ab initio DFT calculations, we characterize the optoelectronic and transport properties of the main subsystems that form the active layer of a prototypical PV solar cell, based on dye/ZnO/AZO interfaces. Firstly, we present a first-principles study of the optoelectronic properties of a natural molecular sensitizer namely, cyanin (Cya) dye in aqueous solution [1,3], showing that cyanin has good absorption properties, promising for PV application.

Secondly, we report on the functionalization of the non-polar ZnO(10-10) surface upon the adsorption of the chromophore linker, i.e. the catechol anchor group [4]. The resulting type-II staggered interface is recovered in agreement with experiments, and its origin is traced back to the presence of molecular-related states in the gap of metal-oxide electronic structure. A systematic analysis carried out for further catecholate adsorbates allows us to identify the basic mechanisms that dictate the energy position of the gap states. Finally, we demonstrate how the formation of the cyanin/ZnO interface is detrimental for the efficiency of the final cell, despite the promising optoelectronic properties of the single constituents (i.e. ZnO substrate and cyanin dye).

[1] A. Calzolari et al., *J. Phys. Chem. A* **113**, 8801 (2009).

[2] A. Calzolari et al., *J. Chem. Phys.* **132**, 114304 (2010).

[3] O.B. Malcioglu et al., *J. Am Chem. Soc.* **133**, 15425 (2011).

[4] A. Calzolari et al., *J. Am Chem. Soc.* **133**, 5893 (2011).

# METAL AND METAL-OXIDE CORE-SHELL NANOPARTICLES: A DETAILED STUDY ON ASSEMBLING, STRUCTURE AND MORPHOLOGY

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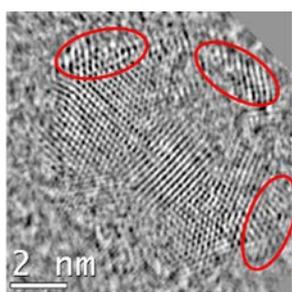
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Fabrication of nanoparticles (NP) with desired shape, structure and size is an important research area, as it presents different and fascinating possibilities, like for instance, improving contrast to enhance Magnetic Resonance Imaging, and realisation of high density memory units. In this work we report studies on various core-shell NP, obtained with an experimental set-up that was recently realised in our laboratories [1]. Preformed metal NP were assembled with a nanocluster gas aggregation source, while oxides shells were obtained with co-deposition in controlled atmosphere of O<sub>2</sub> in the experimental system. We concentrated our studies on Ni@NiO, Ni@MgO and FePt@MgO core-shell NP. Characterization was performed with in-situ X-ray Photoelectron Spectroscopy (XPS) and High Resolution Transmission Electron Microscopy (HR-TEM). Comparison of experimental images with theoretical simulations shows that in all three cases NP core has a regular multitwinned icosahedral structure, composed with single crystal tetrahedra with (111) faces [1]. In order to better investigate the oxide shell, the exit wave reconstruction (EWR) method was applied to the images. NiO phase is clearly observed forming islands on the NP surface. For Ni@MgO NP, in situ XPS and ex-situ Energy Filtered-TEM shows that Ni core remains metallic, whereas Mg, located at the shell, is completely oxidized. Recent results on morphology, structure and magnetic properties of FePt NP embedded in MgO matrix will also be presented.

The system we studied consists of J-aggregated dye (TDBC) in interaction with a surface plasmon on silver. We investigate experimentally the spatial diffusion and coherence with a Young's interferences setup extracting luminescence emission from two different points of the sample [5]. The in-phase emission of regions separated by several microns is observed. These experiments are compared to a system in weak coupling regime where a different behavior is observed. The diffusion and interference experiments in strong coupling regime show that strong coupling leads to a macroscopic quantum state on several micrometers. This effect can be used for long range intermolecular energy transfers and can also offer an easy manipulation of this coherent state by structuring the metal or the organic semi-conductor.

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**Figure 1.** EWR of images taken from Ni/NiO NP with different orientations. The red circles highlight areas with lattice parameters and/or stacking different from the ones of Ni core.

# LARGE SCALE ATOMISTIC INVESTIGATION OF POLYMER-METALOXIDE HYBRID INTERFACES

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We adopt a hierarchic combination of model potential and first-principles atomistic methods to generate realistic models of interface between the polymer poly3hexylthiophene (P3HT) and nanostructured metaloxides such as titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO). Such kind of polymer metaloxide hybrids have emerged as promising systems for photovoltaics. The theoretical understanding of the interface morphology at the atomic scale is of great relevance to improve the properties of such hybrid materials (Seed Project “POLYPHEMO” [1]).

We provide evidence that the polymer organization at the interface (both in vacuo or in presence of typical solvents such as tetrahydrofuran) strongly affects the properties of the system. It is found that the polymer adhesion depends on the curvature at the nanoscale and on the local charge of the metaloxide [1]. Furthermore, the polymer assembling [2] at the interface critically affects the transport properties[3]. The implications on the local transport properties and photoconversion efficiency are discussed.

Wrapping phenomena of P3HT on carbon nanotubes [4,5] and ZnO nanoneedles and their effects on the electronic properties of the hybrids are discussed as well. This work is funded by the Italian Institute of Technology (IIT) under Seed Project “POLYPHEMO” and Regione Autonoma della Sardegna under Project “Design di nanomateriali ibridi organici/inorganici per l’energia fotovoltaica” L.R.7/2007

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# OPTICAL RESPONSE AND ULTRAFAST SPECTROSCOPY OF METAL-BASED HYBRID NANOPARTICLES

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The size, shape and structure dependencies of the properties of nano-objects, and the concomitant possibilities opened to control them, lead to considerable activities in the academic and industrial domains. Confinement effects in nano-objects formed by a single material, e.g., a metal or a semiconductor, have been now extensively investigated.

The optical properties of nano-hybrids, i.e., nanoparticles formed different materials as two metals, or metal - semiconductor, or metal –dielectric are still little studied up to now. The combination of the nanoscale response of their components offer wide ranges of possibilities for developing novel plasmonic systems, and also raise fundamental questions on plasmon-plasmon or plasmon-exciton coupling and on energy and charge transfer mechanisms between the forming materials.

We report here on the optical response of hybrid hammer-like shape nanoparticles formed by a metal (Au sphere) and a semiconductor (CdS or ZnO rod), measured on ensembles and on individuals nano-hybrids. Results are interpreted in terms of dielectric coupling of the two-materials, yielding a good reproduction of the experiments in the non-resonant exciton-plasmon regime.

The ultrafast nonlinear response of these nanohybrids has also been investigated on ensembles using a two-color wavelength-tunable femtosecond pump-probe technique. When carriers are injected in the semiconductor part, a spectral shift of the gold surface plasmon resonance is observed yielding evidence for ultrafast electron transfer between the two-materials. Measurements performed in CdS-Au hybrids, probing the carrier population in the semiconductor part with 40 fs pulses, suggest an upper limit for the electron transfer time of about 20 fs.

Single nano-object investigations have been performed using the far field microscopy technique based developed in our group (SMS, Spatial Modulation Spectroscopy). This permits detection of a single nano-object and quantitative measurements of its linear extinction cross-section and ultrafast response. As an application, we will show how the contact in core-shell metal – silica nanohybrids (Au@SiO<sub>2</sub>, Ag@SiO<sub>2</sub>) affects their non-linear optical response, and in particular modify the acoustic vibrations of the composite nano-spheres.

# SYNTHESIS AND ASSEMBLY OF COMPLEX NANOCRYSTALS STRUCTURES

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Current efforts of nanoscale science and technology are related to the fabrication of functional materials and devices in which the individual units and their spatial arrangement are engineered down to the nanometer level. One promising way of achieving this goal is by assembling of colloidal inorganic nanocrystals as the novel building blocks of matter. This trend has been stimulated by significant advancement in the wet-chemical syntheses of robust and easily processable nanocrystals in a wide range of sizes and shapes. The increase in the degree of structural complexity of solution-grown nanostructures appears to be one of the directions towards which nanoscience will increasingly orient. The talk will highlight the recent advances in the synthesis of colloidal nanocrystals, with emphasis on the strategies developed in our group for the fabrication of colloidal nano-heterostructures, as well as on their properties and their assembly into both ordered and disordered architectures. Particular attention will be devoted to the driving forces involved in nanocrystal assembly. More specifically, we will describe a peculiar hierarchical assembly pathway followed by hybrid octapod-shaped nanocrystals. These nanoparticles were found to self-assemble, in a suitable solution environment, in two sequential levels. First linear chains of interlocked octapods were formed, and subsequently these chains spontaneously self-assembled into three-dimensional superstructures. All the instructions for the hierarchical self-assembly are encoded in the octapod shape. We also demonstrated that the mechanical strength of these superstructures is improved by welding the constituent nanocrystals together. The sequential steps of synthesis of complex building blocks, their hierarchical assembly and their welding can be considered as a novel route towards the realization of ordered mesostructures by a completely bottom-up approach.

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# STRUCTURAL AND OPTICAL PROPERTIES OF A HYBRID NANOCOMPOSITE COMBINING DYES AND AG NANOPARTICLES IN A BLOCK COPOLYMER MICELLE

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Over the past years, hybrid nanocomposites combining fluorescent organic/inorganic emitters with noble-metal nanoparticles have gained increasing interest. Indeed, engineering plasmon–exciton interaction opens up attractive ways to tailor the electro-optical properties of nanocomposites containing materials with different characteristic. Previous studies mostly investigated hybrids with metal nanoparticle sizes between 10 and 100 nm (in diameter) owing to the large magnitude of the plasmonic effect and small affinity to aggregation. However, only very little effort has been carried on ultra-small nanocrystals, although these are better suited for many applications, e.g. in biology, where a minimal invasive integration is required, as well as in catalysis, (bio)-sensor technology, photovoltaic devices, and nanolasers.

Here, we investigate a hybrid nanocomposite combining superradiant emitting dyes [1] and ultra-small (< 3 nm) silver nanoparticles in a block copolymer micelle. Thereby we can access the intriguing regime in which the dimensions of the nanoparticles and the characteristic energy transfer distance between the dyes are comparable. Although the nanoparticle is significantly smaller than the electromagnetic skin depth, we observe a modification of the radiative lifetime and the non-radiative energy transfer among the dyes. This behaviour is absent in a control experiment with dyes whose energetic levels are far from the plasmonic resonance, establishing the plasmonic nature of the interaction [2].

The combination of inorganic nanocrystals with the organic materials into hybrid systems could enable tailoring the opto-electronic properties at the nanoscale.

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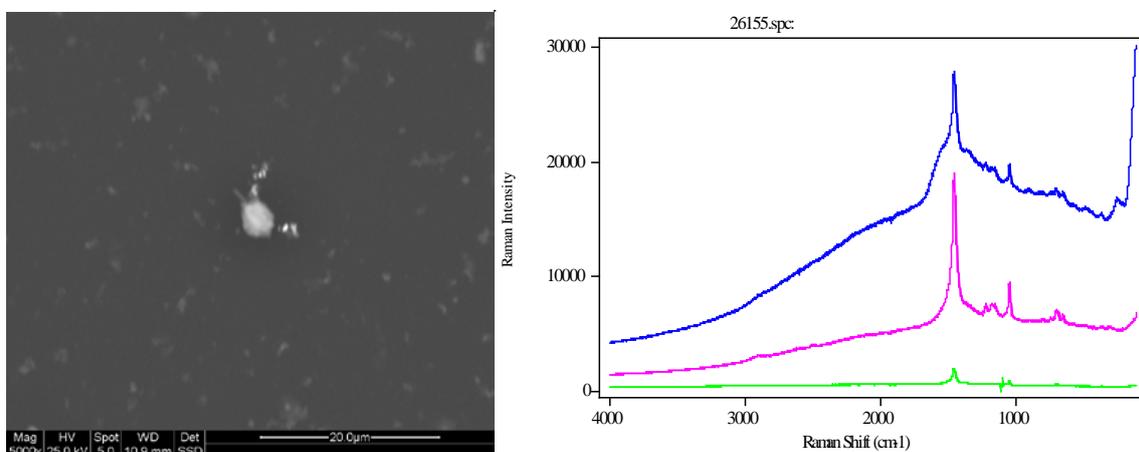
# AG NANOPARTICLES (CHEMI) ADSORBED ON THIOPHENE THIN FILMS GRAFTED ON GLASSY CARBON

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Glassy Carbon and N doped Si(111) surfaces are functionalized yielding hybrid organic/inorganic interfaces. Thiophene derivatives [1] are chemically adsorbed through adsorbate/substrate covalent bond (grafting). Ag nanoparticles (NP) are subsequently adsorbed on the organic layer by simple dipping in a Ag(NP) containing suspension. The grafting of the organics is carried out exploiting electrochemical radical generation (organic halides electroreduction); the photochemically grafting route is also currently tested. The GC/poly-thiophene/Ag(NP) interface is used to study the electrodeposition of Zn on Ag(NP), which is expected to show under potential deposition (UPD). These hybrid systems seem of some interest in both energy (in particular for the oxygen reduction reaction, ORR) [2,3] and sensor application. Screening LA-MS (laser ablation followed by mass spectrometry) and Raman spectroscopy (presenting SERS effect) measurements were carried out to probe the structural properties of these systems, SEM images are recorded to characterize the morphology. Ab-initio calculations are exploited to simulate the relevant physicochemical properties, see for instance [4]. SEM and Raman results (the peak at  $1400\text{ cm}^{-1}$  is tentatively assigned to the CC single bond stretching on the basis of B3PW91/lan12DZ calculations performed on Ag<sub>20</sub>/Br-Thiophene cluster) are shown, left to right respectively.



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# MANIPULATION OF THE DISTANCE BETWEEN GOLD NANOPARTICLES AND A GOLD FILM BY APPLIED POTENTIALS

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Metallic nanoparticles (NP) exhibit strong optical resonances known as localized surface plasmons, which are influenced by their dielectric environment and the presence of nearby metallic structures like other NPs or, in particular, metal films.

We demonstrate a way to manipulate the distance of NPs to a gold film by applying electrical potentials to the film. Functionalized NPs react to the applied potential due to their negative zeta potential: negative electrode potentials repel while positive potentials attract the NPs to the gold film. A reduction of the distance of the NPs to the gold film leads to a stronger coupling of the localized surface plasmon resonance (LSPR) of the NPs and the surface plasmon resonance of the gold film. This results in a red shift of the LSPR.

In order to achieve a reversible and persistent distance modulation, it is necessary to use surface passivation layers (self-assembled monolayers, SAMs) on the gold electrodes. We investigated several SAMs where NPs are bound either by non-specific adhesion or specific protein linkers on top of these layers.

We utilize an inverted microscope with a 100x oil objective (NA 1.4) and a home-built microfluidic cell with lithographically defined gold microelectrodes. Dark field illumination is used to excite the NPs.

Measurements with an electron multiplying (EM) CCD camera and optimized bandpass filters allow us to monitor several NPs in parallel; in response to an applied square wave potential the NPs are lifted off (or drawn to) the surface, which leads to an intensity variation in the EMCCD signal due to plasmon coupling effects.

Plasmon shifts are quantified from single NP spectra.

# SYNTHESIS OF LINEAR AND HYPERBRANCHED METAL-SEMICONDUCTOR HYBRID NANOPARTICLES

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Recent trends in the synthesis and characterization of A<sub>2</sub>B<sub>6</sub> - Au hybrid nanoparticles will be discussed. Uniformly sized gold nanoparticles can be selectively deposited onto the tips of hyperbranched CdTe and rod-shaped CdS nanostructures. These novel hybrid semiconductor-metal nanostructures may be useful for energy conversion, optoelectronics, and biofunctional platforms.

# SIMULATION OF PARTICLE PLASMONS WITH THE MNPBEM TOOLBOX

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Surface plasmons, the workhorse of plasmonics, allow to bridge between the micrometer and nanometer length scales of conventional optics and nanodevices. This is achieved by binding or converting light to coherent electron charge oscillations, confined to the surface of metallic nanostructures.

In this talk, I will present the Matlab Toolbox MNPBEM which we have developed over the last years and which allows the simulation of particle plasmons in metallic and hybrid nanoparticles [1]. I will investigate the interaction of molecules [2-4] and electrons [5,6] with plasmonic nanoparticles, and will compare our simulation results with experiment.

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# ENERGY TRANSFER IN WEAKLY COUPLED HYBRID NANOSTRUCTURES

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A large effort has been devoted to the successful development of organic light emitting diodes (OLED) despite their intrinsic limitations, particularly regarding carrier injection and transport, as compared to inorganic semiconductor devices. Inorganic-organic hybrid materials may allow the rules that apply to matter and light to be further stretched, potentially seeding a new paradigm in optoelectronic devices taking advantage of the best of both worlds. This is of paramount relevance in the strong coupling regime in which novel hybrid quasiparticles are formed [1], but also in the weak coupling regime, in which Wannier and Frenkel excitons maintain their individuality, an hybrid system offers significant advantages. In particular, a way to circumvent the drawbacks of organic materials mentioned above is to use an heterostructure containing an inorganic semiconductor subsystem in which carriers are electrically injected, transported and bound into excitons, coupled to an organic light emitting subsystem via a Förster energy transfer process. As a step in this direction, it has been proposed and recently demonstrated that non-radiative energy transfer can be efficient enough. Following early theoretical predictions, the energy transfer process has been observed from a quantum well to a quantum dot overlayer, and from a quantum well to an organic overlayer [1].

Here we consider the non-radiative resonant energy transfer from a two-dimensional Wannier exciton (donor) to a Frenkel exciton of a molecular crystal overlayer (acceptor). As most of the organics are anisotropic, we characterize the effect of the optical anisotropy on this process. Using realistic values of material parameters, we show that it is possible to change the transfer rate within typically a factor of two depending on the orientation of the crystalline overlayer. The resonant matching of donor and acceptor energies is also partly tunable via the organic crystal orientation. We use a macroscopic approach that could be easily extended to different geometries and configurations, from quantum well to quantum dots, to microcavities, possibly including plasmonic effects or vibronic progressions.

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# SPIN TRANSPORT AND MAGNETIZATION DYNAMICS IN HETEROGENEOUS NANOSTRUCTURES: A MULTISCALE APPROACH

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The mutual interaction between spin transport and magnetization dynamics in hybrid nano-devices is at the origin of physical effects, such as Spin Transfer (ST) [1] and Giant Magneto Resistance [2], which act at very different length scales, and depend both on the microscopic characteristics of the material and on the geometry of the device. These effects opened a potential for various applications, such as magnetic memories, reprogrammable logic, and Spin Torque Nano Oscillators (STNO) [3].

We report on a theoretical model, based on Continuous Random Matrix Theory (CRMT) [4] and Non Equilibrium Green Functions [5], that describes on an equal footing transport and magnetic degrees of freedom in realistic devices. The model has been implemented in a simulation code [6] that allows one to compute local (spin torque, spin accumulation and spin/charge current) and macroscopic (resistance) transport properties of spin valves. Our approach offers a systematic way to perform multiscale simulations [7] in heterogeneous systems with arbitrary geometry, connected to an arbitrary number of electron reservoirs. Bulk and interface properties of very different materials (magnetic and non-magnetic metals, insulators, semiconductors, superconductors) are properly captured by our model, which can be parametrized using both experimentally accessible parameters and ab initio calculations.

As an application of our method, we have coupled CRMT to a micromagnetic simulation code, in order to model a spectroscopic experiment [8], based on a mechanical detection of the ferromagnetic resonance, and performed on a STNO. Our simulations predict correctly the selection rules for spin wave modes excited by ST, and give a description of the complex dynamics of the magnetization in qualitative agreement with experiments.

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# MULTIFUNCTIONALIZED GOLD NANOPARTICLES FOR SMART INTRACELLULAR DELIVERY BY NON-LINEAR EXCITATION

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Gold nanoparticles offer a most suitable platform for the development of modular nano devices. On one hand their surface properties enable effective coating by peptides yielding stable and non-cytotoxic systems. On the other, their intriguing photophysics, characterized by the surface plasmon resonance, can be exploited for novel excitation schemes. Here we report the design of nanosystems for the controlled intracellular release exploiting both these features.

We use a single-step method to coat and functionalize water-dispersed gold nanospheres (AuNss) with different peptides containing a cysteine residue at their N-terminal, thereby yielding, on a single nanostructure, distinct reactive groups decided by the C-terminal amino acid. The structures are further stabilized through the formation of a Self-Assembled Monolayer (SAM) on their surface, driven by the interactions among the hydrophobic regions of the peptides. The resulting nanoparticles present reactive click-chemistry groups on their surface enabling rapid, selective, and modular conjugation to virtually any chosen biomolecule or fluorophore.

Furthermore, thanks to the ability to produce a photolabile 1,2,3-triazole moiety between the coating and the payload, we achieved photocontrolled release by 561 nm laser excitation. The release mechanism exploits multiphoton cleavage of the triazolic ring triggered by the local EM field enhancement due to excitation of the AuNs surface plasmon. Thanks to the multiphoton excitation, this novel system enables the photocleavage of UV labile groups by yellow-green light at low excitation power ( $\mu\text{W}$ ), thereby improving tissue penetration and reducing photodamage.

# ONE-SIDED GROWTH OF LARGE PLASMONIC GOLD DOMAINS ON CdS QUANTUM RODS OBSERVED ON THE SINGLE PARTICLE LEVEL

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The synthesis of 'hybrid' nanocrystals composed of domains from different material classes (e.g. magnetic, semiconducting, metal) represents a challenging field in material science. The multiple components of such nano-sized hybrid crystals provide several physical-chemical functionalities within one structure and novel properties are expected via the electronic and electromagnetic coupling between the components. The two most important phenomena arising in nanostructures and altering their electronic and optical properties are quantum confinement in semiconducting nanocrystals (quantum dots) leading to a size tunable band-gap and the electrodynamic confinement in (plasmonic) metal nanocrystals leading to high polarizability at the plasmon frequency. The coupling of plasmons and quantum confinement in metal-semiconductor hybrid systems is poorly understood, mainly due to the difficulty to prepare such systems. Potentially the plasmonic 'antenna'-effect could amplify the excitation or radiative decay of excitons in the semiconductor.

Only a few years ago, the controlled crystallographic growth of small gold crystals selectively on the tips of rod-shaped semiconducting nanocrystals emerged, where the metal is in direct crystallographic contact with the semiconductor. Those structures showed a switch from two-sided to one-sided growth attributed to intraparticle electrochemical Oswald ripening. Those 'dumbbell' or 'matchstick' particles were used for directed self-assembly and it was shown that electrons created in the semiconductor by optical excitation transfer and accumulate on the gold tip where they are able to reduce organic molecules. So far, it has not been possible to control the size of the gold domain in those metal-sc hybrids. The gold domains were typically in the order of 1.5-3.5 nm in diameter. Since plasmons in gold nanoparticles are strongly damped for particle diameters below 10-20 nm by surface scattering and the size dependent d-band-Fermi-level offset, the poorly understood interaction between plasmons and excitons could not be studied in detail so far.

We present a strategy to create large gold domains (up to 15 nm) on CdS or CdSe/CdS quantum rods. The gold domain is large enough to support efficient plasmon oscillations, which leads to a high optical scattering and absorption cross section. The light scattering cross section is large enough to visualize single hybrid particles in a dark-field microscope during the particle growth in real time, which gives new insight into the electrochemical processes involved after photo-excitation of metal-semiconductor hybrid particles.

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# HYBRID FUNCTIONALS AND GW CORRECTIONS TO QUANTUM TRANSPORT CALCULATIONS

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The unprecedented technological development in the microelectronics industry eventually arrives at its ultimate limit when individual electronic devices reach the nanoscale. The design of these systems will rely on an accurate quantum-mechanical ab-initio modeling of electronic transport through them.

The non-resonant tunneling regime for charge transfer across nanojunctions is critically dependent on the so-called beta parameter, governing the exponential decay of the current versus the length of the junction. For periodic materials, this parameter can be theoretically evaluated by computing the complex band structure (CBS) - or evanescent states - of the material forming the tunneling junction. In this work [1] we present the calculation of CBS for organic polymers using a variety of computational schemes, including standard local/semilocal DFT and hybrid DFT functionals. We validate the computed electronic structure wrt state-of-the-art GW calculations.

We also directly address the description of the interface electronic structure in a prototype metal-organic nanojunction. We perform [2] many-body perturbation theory calculations at the GW level, as compared with a state-of-the-art DFT treatment. Such corrections seem to be critical for a quantitative evaluation of transport properties and are found to be important to describe the metal-molecule hybridization.

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## **ABSTRACTS OF POSTERS**

# LOCALIZATION OF ELECTRON AND HOLE GAS IN HEXAGONAL CORE-MULTISHELL NANOWIRES

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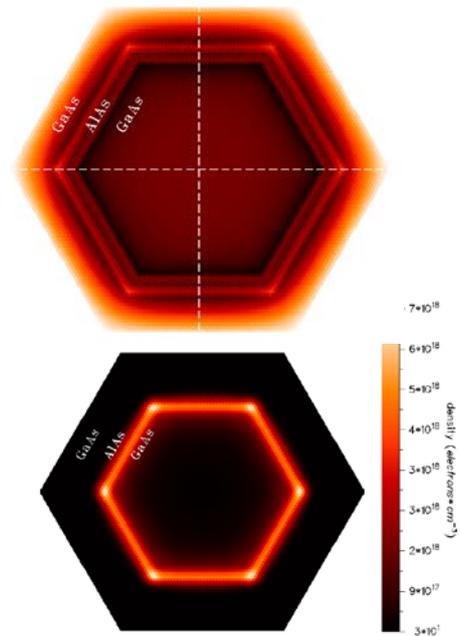
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Multishell coaxial semiconductor nanowires are attracting much interest due to their possible application as light harvesting devices [1], nanophotonic sources [2], and nanoscale FETs with novel geometries [3]. Their cross-section usually reflects the prismatic crystallographic arrangement and can hardly be considered circular. In particular, III-V nanowires often show an hexagonal shape, with the embedded curved 2DEG wrapped on the surface of the prismatic hexagonal interface between different materials. The inclusion of the 2DEG shape in the calculation of electronic states is thus of primary importance since it leads to localization of carriers on the corners of the hexagon [4]. Here, we study how the self-consistent band profile induces the formation of shallow channels for electrons along the edges, and show how the system geometry and doping profile tailor the mutual coupling of such 1D regions.

We consider a prismatic nanowire with hexagonal cross section [5,6]. The internal GaAs core is covered with an AlAs uniform layer and another GaAs layer. A thin layer of dopants (nominally a delta-layer doping) is introduced in the middle of the AlAs region. The figure on the right shows the conduction band and the electron density in color-code in the upper and lower graphs, respectively: darker means lower energy/density. An edge of the hexagon is 66 nm long and the simulation is at 4 K temperature.

We find different localization regimes for electrons and holes [7]. In particular, conduction-band electrons form six 1D channels along the corners, whose mutual coupling can be tailored by the sample geometry and doping density.



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# DESIGNING ALL-GRAPHENE NANO-JUNCTIONS BY EDGE FUNCTIONALIZATION: OPTICS AND ELECTRONICS

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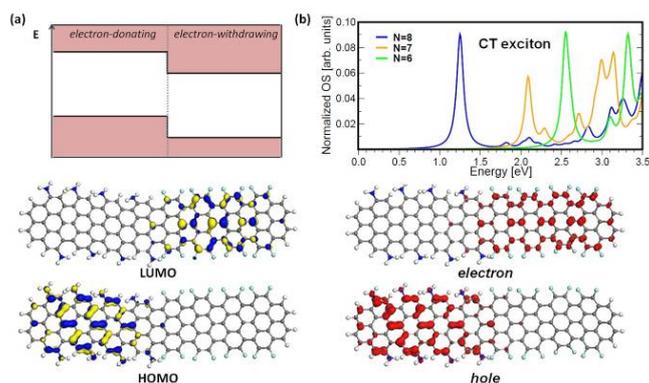
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The most recent developments in bottom-up experimental techniques allow to produce nowadays sub-nanometer wide graphene nanoribbons with atomistic control on their shape and termination [1]. We investigate the effect of edge covalent functionalization on the opto-electronic properties of realistic graphene nano-flakes (GNFs) and junctions (GNJs). By means of well tested semi-empirical methods [2], we compute for the optimized structures both mean-field ground state electronic properties and configuration-interaction optical excitations. Our study shows that functionalization can be designed to tune electron affinities and ionization potentials of GNFs [3]. This effect can be exploited to realize both type-I (straddling) and type-II (staggered) all-graphene nano-junctions. At variance to type-I, we find that type-II GNJs can display indirect excitations with electrons and holes localized on different sides [4]. The optical properties are characterized in terms of size and functionalization. Nanoplasmonic effects of elongated GNFs are also discussed [5].



**Figure 1:** (a) Scheme for *type-II* GNJ: electron-withdrawing termination down-shifts the gap region with respect to electron-donating one: frontier orbitals are localized on opposite sides of the junction; (b) UV-vis spectra of GNJs at increasing width: the first peak presents charge transfer character, as shown by the computed *electron* and *hole* densities.

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## DIRECTIONAL SENSITIZATION OF ZnO NANORODS BY TiOPc SUPERSONIC BEAM DEPOSITION

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The ability to control the formation of hybrid structures at the nanoscale is crucial to determine specific properties and unique characteristics of the nano material. With this aim, we selective functionalize ZnO nanostructures, with organic oligomers, using Supersonic Molecular Beam Deposition (SuMBD), applying the directional properties of the seeded supersonic beams to the growth. In recent years SuMBD has been successfully used as a high controlled growth technique for organic oligomer thin films [1], with unique properties in structural and morphological order [2] and consequently improved performances in devices applications [3]. Based on the supersonic expansion of a seeded carrier gas, SuMBD present properties of high kinetic energy of the molecules and highly focused and directional beams. We applied SuMBD to ZnO nanorods [4], which present interesting advantages. First of all, ZnO nanorods present a continuous crystalline structure, which could be grown on a conductive transparent metal oxide (TCO) made ZnO doped with Aluminium (AZO) deposited directly on glass [5]. In such a way, the structural homogeneity and crystalline properties are maintained all over the NR length, allowing a continuous path for the electrons in the material. The selective functionalization with Titanyl Phthalocyanine by SuMBD on each single nanorod has been achieved. Using the directional properties of the beam a selective growth on one side of the nanorod has been realized. We characterized the morphological and structural properties of the nanohybrids using HR TEM, and local chemical analysis. The optical characterization using photoluminescence have been performed. The directional selective functionalization of ZnO nanorods with phthalocyanine molecules could be useful in many applications, for example in DSSC to improve solar radiation absorption, using different molecules on different sides of the nanorods.

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# CHARGE TRANSFER DYNAMICS IN FERROCENE MOLECULAR ARCHITECTURES GRAFTED ON Si(111)

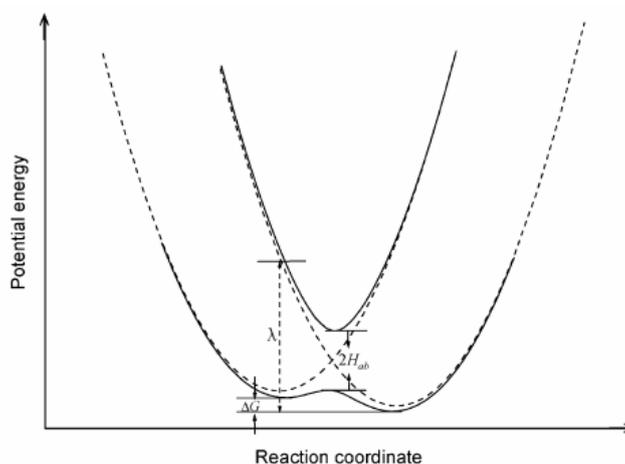
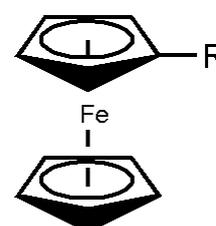
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Various experimental strategies are exploited to graft Si(111) surfaces aiming to realize hybrid – Si(111)/organic spacer/metallic center – interfaces. The Ferrocene redox couple on the Si(111) surface is grafted exploiting photochemical grafting, surface chemical reaction using a Pt catalyst and post functionalization of Si(111) surface previously modified with undecanoic acid. In the left figure consider the substituent as being R = –H (FC), –CH<sub>2</sub>–OH (MFC), –CH=CH<sub>2</sub> (VFC). Cyclic voltammetry and electrochemical impedance spectroscopy are used to characterize experimentally the grafting process and the surface state. In particular, the dynamics of the electron transfer is assessed as a function of different Si(111) - molecular spacer - ferrocene architectures. This hybrid interface is also characterized exploiting various techniques, such as Cyclic Voltammetry, MALDI-TOF, LA-ICP-MS. Eventually, the so-called matrix element, 2H<sub>ab</sub>, values are theoretically reckoned to determine the charge transfer rate constant, aiming to compare theoretical vs experimental (CV simulation) charge transfer rate constant values.



# ELECTRON SCATTERING BY INTERFACE PHONONS IN A POLAR METAL-OXIDE-SEMICONDUCTOR DEVICE

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We consider a metal- oxide- semiconductor (MOS) capacitor in a macroscopic description as a multilayer system. Each layer is characterized by a different dielectric function [1]. For a polar semiconductor, e.g., the III-V InGaAs, the plasmon dielectric response, due to a collective excitation of the conduction band electrons, is complemented by one due to optical phonons [2].

The different dielectric permeabilities give rise to polarisation charges on the interfaces, and hence a polarisation potential that extends into the semiconductor layer. The length scale of the penetration is tens of nm, comparable to channel widths in modern MOS field effect transistors (FETs). Hence, electrons injected into the channel can be scattered by the interface polarisation potential.

In current 20nm feature size and smaller devices, "high-k" oxides, e.g., HfO<sub>2</sub> with higher dielectric constant than SiO<sub>2</sub>, have replaced the native Si oxide, because they reduce gate leakage currents. In III-V (InGaAs) MOSFETs, which promise increased channel carrier mobility, there is a further disadvantage to the native oxide: It gives rise to interface states, which pin the Fermi level and prevent proper transistor switching. This can be resolved by replacing the native oxide with a thin layer of the low dielectric oxide Al<sub>2</sub>O<sub>3</sub> [3]. Moreover, since interface phonon scattering is expected to be larger for higher oxide dielectric constants<sup>1</sup>, and vice versa, the presence of Al<sub>2</sub>O<sub>3</sub> at the channel-oxide interface may reduce carrier scattering due to interface excitations.

We calculate the effect of interface phonon-plasmon scattering on channel carrier mobility in this structure using a continuum polarization model of the multi-layer dielectric and an effective mass treatment of the carrier wave functions in the channel. We compare the scattering of carriers with and without the Al<sub>2</sub>O<sub>3</sub> layer, and make an estimate for the contribution of electron-plasmon scattering by investigating two limiting cases: (1) treating carrier-plasmon and carrier-phonon scattering on the same basis, (2) completely neglecting plasmon effects in the dielectric functions. The first model is expected to overestimate plasmon scattering, because the momentum transferred from electrons to plasmons may be reabsorbed, whereas the second approach, ignoring plasmons entirely, underestimates it.

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# FULLY DOPED EMERALDINE OLIGOMERS: A THEORETICAL STUDY OF THE OPTICAL PROPERTIES

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Conjugated organic polymers can be doped (via oxidation/reduction chemistry, or acid/base chemistry) to induce high electrical conductivity. Polyaniline (PANI) increases remarkably its conductivity by means of proton-acid doping, reaching values of the order of  $10^2$  S/cm [1]. This makes PANI particularly perspective for organic electronics applications in electronic and opto-electronic devices. The conversion between the neutral semioxidized (emeraldine base, semiconductor) and the doped (emeraldine salt - ES, conductor) form is a reversible and easily controllable process. Alongside with conductivity change, it is accompanied by notable variations of color and magnetic susceptibility.

This study addresses the optical properties of model HCl-doped ES oligomers. The polaron and bipolaron configurations [2] at each chain length are considered. CC2/SVP/COSMO and CIS/6-31G\*/PCM are employed. The choice of protocol is based on earlier findings [3], proving its potential for adequate description of the structure and electron distribution in ES. Parallel CC2/SVP simulations in vacuum are performed in order to estimate the solvent effect on the electron spectra. CC2/SVP/COSMO calculations with a limited amount of explicit water molecules added to the model are carried out as well.

The effect of chain length, counterions position and multiplicity on the electronic spectra is traced with special emphasis on the comparison between bipolaron and polaron forms. The results provide detailed information about the possible electron transitions in ES. The MO analysis affords description of the polaron/bipolaron states. The nature of the molecular orbitals involved in electron transitions and size dependence of the optical spectra are discussed. The simulated spectra are compared to the available experimental data.

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## AZOBENZENES SELF ASSEMBLED MONOLAYERS

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The photoisomerization process of azobenzene is widely studied both in solution and on metal surfaces [1,2], because of its efficiency and controllability. These features make the SAM of azobenzene and its derivatives (azo-SAM) a promising tool for controlling the movement of nano-objects with light. In a recent work a classical MD simulation of the isomerization process in solution has been performed by exploiting a sampling of both the Excited- and Ground-State Potential Energy Surfaces (PES) [3]. Prompted by these results a dedicated force field has been developed for thio-azobenzenes, in order to simulate the isomerization process of an azo-SAM on a metal surface.

To this aim, a detailed sampling of the potential energy surfaces (PES) function has been done by means of QM methods, then force field parameters have been obtained by minimizing the difference between the QM-PES and the MM-PES. The robustness of parameter set has also been tested against different set of atomic charges obtained by different flavours of the RESP procedure.

Based on this force field, a preliminary study on structural properties of a thio-AZO self assembled monolayer (SAM) on gold (111) surface is presented in this work. Moreover, using a literature force field [4], we have studied the mechanical stiffness of the monolayer in the cis- and in the trans- form. Calculated results agree with available experimental data, notwithstanding the approximations inherent in the modelling.

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# PLASMON COUPLING EFFECTS BETWEEN GOLD NANOSPHERES AND GOLD FILMS

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Metal nanoparticles are ideal reporters for changes in the optical properties of their nano-environment, which cause a shift in the particles plasmon resonances. This resonance shift gets more pronounced if the nanoparticle approaches other plasmonic structures, so that even sub-nanometer modifications in the geometrical configuration can be detected by monitoring the NP plasmon resonance.

Here we investigate single gold spheres (40 nm diameter) on a thin gold film (50 nm thickness) which are interlinked with biomolecules. By applying potentials we are able to modulate the distance of the charged NPs to the film. The sample is installed within a microliter flow-cell, which fits to an inverted microscope with dark field illumination. RGB-images of single particles show, that at attractive potentials the localized surface plasmon resonance (LSPR) of the NPs shifts from green to orange. Simultaneously, the far-field scattering image changes as the NP approaches the surface: around the initial point spread function a differently colored and doughnut shaped intensity profile appears. Repulsive potentials set the NPs back to their initial state. This process is reversible and persistent over many cycles. Spectra of individual NPs also reveal the red-shift of the particle resonance, when the NP-surface distance is decreased.

The LSPR-shifts can be explained with the concept of image charges. These are induced in the metal film by the oscillating electrons of the NP-plasmon, so that the system can be treated as two coupled spherical NPs.

# VALENCE BAND MIXING OF CUBIC GaN/AlN QUANTUM DOTS

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In this work we present a six-band Burt-Foreman Hamiltonian in cylindrical coordinates describing the valence band structure of zinc-blende nanostructures grown along the [001] axis [1]. The Hamiltonian properly includes position-dependent Luttinger parameters and axial magnetic fields. Using this Hamiltonian, we investigate the composition of the hole ground state in GaN/AlN quantum dots (QDs) [2,3] as a function of the dot geometry and external fields. In QDs with small aspect ratio heavy-hole mixing with light-hole and split-off subbands is weak and the ground state is essentially a heavy hole with well defined spin. This makes the system suited for optical manipulation and storage of spins. When the aspect ratio increases, mixing with light-hole and split-off subbands becomes significant and the ground state becomes increasingly sensitive to QD anisotropy, which further enhances the mixing. The use of magnetic fields to manipulate the electronic structure of typical QDs is also investigated. We show that an efficient magnetic modulation of the electronic structure is feasible in QDs with aspect ratio  $\sim 1$ , which can be used to manipulate the optical emission characteristics (energy, polarization, intensity).

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