Publishable executive summary

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Partners of the SA-NANO consortium

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2. The Ruprecht-Karls-Universität Heidelberg, Heidelberg
3. The Ludwig Maximilians University, Munich
4. The Hebrew University of Jerusalem
5. The Tel Aviv University
6. The Laboratoire de Chimie de Coordination-CNRS
7. Institute of Molecular and Atomic Physics of the National Academy of Sciences of Belarus **(new partner)**
8. Photochemistry Center of the Russian Academy of Sciences **(new partner)**

Project web site

www.sa-nano.it

Project Objectives

SA-NANO aims to achieve control and understanding of self assembly of shape controlled colloidal nanocrystals (NCs). NCs have been widely developed during the last decade and already applications in diverse technological fields have been demonstrated, such as light-emitting diodes (LEDs),[1] biological tagging,[2-7] sensing,[8-10] photovoltaics[11,12] electronics,[13] and catalysis.[14] Recently, new synthetic methods were developed for growing NCs with elaborate shapes such as rods[15-17] and tetrapods.[18,19] Rods and tetrapods, generally termed as 'shape controlled nanocrystals', with diameters in the range of 2-10 nm and lengths spanning 10-100 nm, are the focus of this project. We know that only a self assembly approach is going to be applicable to create complex systems with millions or even billions of nano-components, and this is where the project will make a significant contribution. Such assemblies, which are being developed in the SA-NANO project, are interesting both in basic research, as they present a new platform on chemical and physical interactions of proximal nanocrystals, and for practical applications as they pave the way to new materials and to new functional devices. The specific S&T objectives of the SA-NANO STREP project are:

The synthesis of a new generation of shape- and composition- controlled nanocrystals with specific recognition elements and their surface functionalization (Workpackage 1). Shape-controlled growth with topological control are being developed to grow nanorods and tetrapods

with metal, semiconductor, and oxide tips that will serve as anchor points. The new hybrid nanocrystals will be functionalized with biomolecules for purposes of self assembly.
The self assembly of shape-controlled nanocrystals in solution to form chains, propellers and three-dimensional structures of rods and tetrapods (Workpackage 2). The specific linking to Au tips on rods and tetrapods using molecular and bio-molecular bonding will be employed to generate chain-like assemblies of rods. Propeller structures will be realized by attaching rods to a central tetrapod. 3D assemblies of tetrapods linked through their tips will also be realized.
The preparation of substrates patterned with nanocrystal templates of several materials as anchoring points, and assembly of shape-controlled nanocrystals on such substrates (Workpackage 3). Patterned substrates will be fabricated with repeating motifs capable of selectively binding shaped nanocrystals. Ordered groupings of nanocrystals of different materials and sizes are envisioned. Nanocrystals will be assembled onto these patterned surfaces.
T*he realization of aligned assemblies of nanorods* (Workpackage 4). Various methods to align nanorods will be developed including the use of external fields and microfluidics. Deposition of rods on patterned surfaces will be combined with the alignment techniques.
The study of proximity effects on the electronic & optical properties of shape controlled NCs (Workpackage 5). Collective properties of nanocrystals in the assemblies will be studied by optical, magnetic and scanning probe techniques. In particular, the modification of the NC level structure due to proximity to neighboring NCs and the onset of super-crystal effects will be addressed. The effect of alignment leading to anisotropic optical, magnetic and transport ensemble behavior will be investigated. Electronic structure and conduction along rod chains will be studied.
Theory and modeling of self assembly of shape-controlled nanocrystals (Workpackage 6). Various theoretical tools will be developed to model the self assembly processes of rods and tetrapods. We will address issues related to the effects of shape, size, anisotropy, solvent and external perturbations on the resulting assemblies. Theoretical calculations will be performed in order to investigate the electronic and the optical properties of isolated and assembled nanocrystals.

Work performed during the last year

Workpackage 0.
The main result from this WP was the fulfillment of the mid-term assessment criteria, through successful evaluation of the mid-term assessment report and meeting. We also had another internal meeting.

Workpackage 1.
The main achievements for WP1 during the second year are the realization of a wide variety of nanocrystals with anchoring points, as well as the tailored functionalization at their tips for some of them. We have done this also for several materials or combinations of them that were unscheduled at the beginning of SA-NANO. We have studied in detail water solubilization procedures for many of them, and also examined their water stability.

Workpackage 2.
Here, we have successfully obtained chains of AAA type nanocrystals, using avidin-biotin chemistry, studied the non-specific attachment in detail, and also developed a methods for making chains of rods and networks of tetrapods without the use of biomolecules.

Workpackage 3.
Here we have optimized the fabrication of nanostructured surfaces, with gold, silver, platinum or cobalt nanocrystal patterns, which we used to direct the assembly of several types of nanocrystals,

such as dimers, dumbbells and tetrapods. Gold, platinum and cobalt nanoparticles on the substrates have been used for the direct growth of nanorods directly on the substrate, instead of immobilizing them. We also worked on the organization of shape-controlled nanocrystals using block copolymer micelles. Finally, We have tried to grow Co nanorods directly in the aligned channels of porous alumina.

Workpackage 4.

We have worked on assembly of CdSe and CdSe/CdS nanorods from slowly evaporating solvents, with and without electric fields, as well as using drying-mediated evaporation at the air-water interface. We have achieved both lateral and vertical alignment of nanorods over areas of several square microns. We have also continued the efforts of Co nanorods alignment on magnetic substrates. A special set-up is now prepared in our lab in a way to use the strong external magnetic field of an electromagnet for this purpose. We made considerable progress in achieving long-range directional order in InAs nanord arrays.

Workpackage 5.

We have further pursued their scanning tunneling spectroscopy investigation of two-dimensional (2D) InAs quantum-dot arrays and observed the onset of a 2D mini-band level structure in this "quantum-dot solid" system. We have also studied 2D assemblies of locally-aligned CdSe nanorods. In contrast to the case of InAs nanorods, the bandpgap of the CdSe nanorods within the assembly showed (commonly) only a negligible reduction compared to the isolated nanorods. We extended the investigation of the local conductance properties of 3D CdSe quantum-dot assemblies and studied the temperature dependence of the local conductance and local phototransport properties We have continued the studies in order to interpret the magnetic behaviour of the organized bare Co nanorods. Also, we continued the transport measurements on single nanocrystals in electrode junctions.

Workpackage 6.

We have developed several models to address the self-assembly of nanoparticles. We are at the stage of finalizing the best model in terms of computational effort and correspondence with experimental results of HUJ and CNR-INFM. We have also applied the model to study the drying-mediated self-assembly of nanorods under different evaporation conditions, different diffusion rate, different rotation rates, and different interaction parameters. Also, we have finalized the density-functional tight-binding parametrizations for CdSe and CdTe, we have implemented the spin-orbit coupling in the DFTB code, we have implemented a **k·p** code for zincblend and wurtzite heterostructures, which can be easily extended to three-dimensional systems, we have studied the electronic and the optical properties of asymmetric core-shell nanocrystals using the DAVMASS code, and finally, we have developed an envelop function model to describe inter-rod interaction and analyze the optical properties of organized arrays of crystals.

Expected end results, intentions for use and impact

The new assemblies of rods and tetrapods, created by self assembly and developed throughout the SA-NANO project, will exhibit novel properties stemming from the interactions between the nanoobjects and from their collective behavior. All these properties have never been investigated before in the case of shape-controlled nanocrystals. The development of controlled and aligned rod assemblies, for instance, will allow us to examine for the first time the evolution of the level structure and single electron charging energy with the distance between neighboring nanorods. The coupling between NCs, resulting from wavefunction overlap between nearest neighbors, may

reduce the charging energy and modify the level spectrum, as compared to the isolate NCs. Moreover the coupling between transition dipole of NCs may cause the formation of exciton bands. Anisotropic conduction is also expected to be observed along versus perpendicular to the alignment direction.

These structures, once realized and once collective effects are elucidated and rationalized, will clearly show properties and performances that will be *predictable and controllable*. One example will come from assemblies of semiconductor nanorods. Unlike ordered mutilayers of spherical nanocrystals, in which the orientation of each individual nanocrystals is poorly defined, ordered arrays of nanorods will clearly show coherent and unidirectional orientation of all nanorods along a given direction. This well defined geometrical arrangement, coupled with the anisotropic physical properties of the individual nanorods (i.e. linearly polarized absorption and emission), will be translated into a unique and predictable macroscopic property of the ensemble. This ensemble will be, for instance, a flat surface showing highly polarized absorption and emission.

Materials and systems with predictable composition and structure will open the way to *concrete applications*. In the example cited above, one for instance can envisage novel optical detectors and emitters. Assemblies of magnetic nanorods are also expected to yield novel collective magnetic effects that will be unraveled here. As for what concerns tetrapods, ordered arrays on patterned substrates will facilitate the optical, transport and scanning probe investigation of their unique electronic structure. Tetrapods are being exploited as components in thin-film photovoltaic devices where they are incorporated in a host matrix made of a conductive polymer. Low-cost photovoltaics is today regarded as one of the promising applications of nanocrystals. Needless to say those photovoltaic devices have also tremendous advantages with respect to the environmental impact in energy conversion.

Ordered assemblies of shape-controlled nanocrystals will also be useful in catalysis. Shape-controlled nanocrystals are grown such that certain crystallographic facets have much larger surface area than others. Such facets might have higher catalytic activity towards the photodegradation of some pollutants. The possibility of growing composite nanocrystals, such as the metal-tipped nanorods and tetrapods, will enhance this activity even further. In these materials separate redox processes will likely occur in different regions of the nanocrystal, thus vastly enhancing the catalytic activity, as has been demonstrated in metal-patched TiO_2 nanocrystals. Networks of tetrapods (or of other three-dimensional shaped nanocrystals), either free-standing or supported on a surface, could then serve as media for the rapid degradation of pollutants.

As can be clearly seen, the goals of SA-NANO aim to transform the versatility of the individual objects to large scale ensembles that hold a considerable potential for industrial applications.

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