Project no. STRP 013698

Project acronym: SA-NANO

Project title: Self Assembly of Shape Controlled Colloidal Nanocrystals

Instrument SPECIFIC TARGETED RESEARCH PROJECT

Thematic Priority Nanotechnologies and nanosciences, knowledge-based multifunctional materials, and new production processes and devices

Final Publishable Activity Report

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Project coordinator name **Liberato Manna**
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Table of Contents

1. Executive summary

Coordinator Contact Details

Dr. Liberato Manna
National Nanotechnology Laboratory of CNR-INFM
Distretto Tecnologico - Isufi
Via Arnesano Km 5, 73100 Lecce, ITALY
Email: liberato.manna@unile.it
Tel +39 0832 298 207
Fax +39 0832 298 238

Partners of the SA-NANO consortium

1. The National Nanotechnology Lab of CNR-INFM
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. The Stepanov Institute of Physics of the National Academy of Sciences of Belarus
8. The Photochemistry Center of the Russian Academy of Sciences

Project web site

www.sa-nano.it

Project Objectives

SA-NANO has aimed 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, have been 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 has made a significant contribution. Such assemblies, which have been 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 were:

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 have been developed to grow nanorods and tetrapods with metal, semiconductor, and oxide tips that have served as anchor points. Many of these new hybrid nanocrystals have been functionalized with biomolecules for purposes of self assembly.

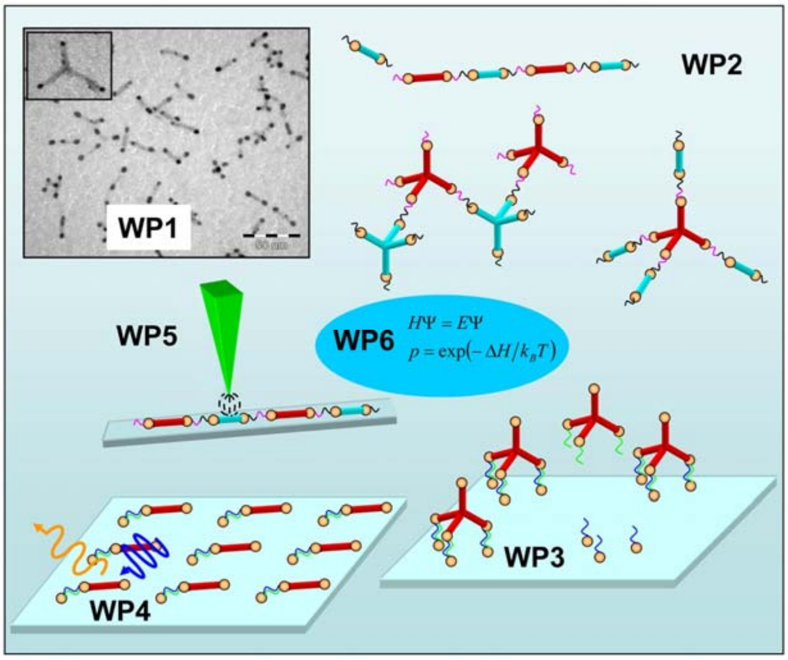
The self assembly of shape-controlled nanocrystals in solution to form chains, propellers and three-dimensional structures of rods and tetrapods (Workpackage 2). The specific linking to Au tips on shape-controlled nanocrystals, in some cases using molecular and bio-molecular bonding, has been employed to generate chain-like assemblies of rods and 3D networks of tetrapods. Propeller structures have been realized by a nano-welding approach that involved the coalescence of Au domains on the tips of bullet-shaped nanocrystals.

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 have been fabricated with repeating motifs capable of selectively binding shaped nanocrystals. Nanocrystals have been assembled onto these patterned surfaces.

The realization of aligned assemblies of nanorods (Workpackage 4). Various methods to align nanorods have been developed including the use of external fields and microfluidics. Deposition of rods on patterned surfaces has been combined with the various 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 have been 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 has been addressed. The effect of alignment leading to anisotropic optical, magnetic and transport ensemble behavior has been investigated. We have also attempted to study the electronic structure and conduction along rod chains.

Theory and modeling of self assembly of shape-controlled nanocrystals (Workpackage 6). Various theoretical tools have been developed to model the self assembly processes of rods and tetrapods. We have addressed issues related to the effects of shape, size, anisotropy, solvent and external perturbations on the resulting assemblies. Theoretical calculations have been performed in order to investigate the electronic and the optical properties of isolated and assembled nanocrystals.



Scheme 1: Graphic representation of the main S&T objectives of the SA-NANO STREP project. In WP1 Au-tipped rods and tetrapods have been developed and funtionalized. A TEM image with rods onto which gold was selectively grown is shown, while the inset shows a tetrapod with gold tips. WP2 has developed self asssembly of rods and tetrapods in solution such as rod chains, tetrapod-rod propellers and 3D tetrapod assemblies. WP3 has focused on arranging rods and tetrapods onto pre-patterned substrates. WP4 has developed rod assemblied driven by external biases. In WP5 the collective properties of rods in assemblies have been studied by spectroscopy and scanning probe microscopy. WP6 has dealt with the theory of self assembly and the electronic structure calculation and will have a strong interaction with all the other workpackages.

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, have exhibited novel properties stemming from the interactions between the nano-objects 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, has allowed us to examine for the first time the evolution of the level structure and single electron charging energy with the distance between neighboring nanorods. In many cases we have found that the electronic coupling between NCs, resulting from wavefunction overlap between nearest neighbors, reduces the charging and confinement energies and modifies the level spectrum, in particular the band-gap, as compared to the isolated NCs. Moreover, in extreme cases such a coupling causes the formation of collective array mini-bands, as demonstrated for InAs NC arrays. Anisotropic conduction is also expected to be observed along versus perpendicular to the NC alignment direction.

These structures, once realized and once collective effects have been elucidated and rationalized, have clearly shown properties and performances that to some extent were *predictable and controllable*. One example comes 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 have clearly shown 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), has been translated into a unique and predictable macroscopic property of the ensemble. This ensemble was, for instance, a flat surface showing highly polarized absorption and emission, but also strong directionality in the emission of light.

It is important to stress that 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. 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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2. General Project Objectives and project’s current relation to the state-of-the-art

The SA-NANO consortium was established among several European research institutions with the aim to advance the self assembly of shape-controlled nanocrystals. The SA-NANO STREP project, which was started in February 2005, has now come to its end. The main focus of the project has been on rods and tetrapods, which have been developed so as to posses a functional part and a recognition element for the purposes of self assembly. Gold/ semiconductor/ metal oxide / magnetic tips have been selectively grown on the edges of rods and tetrapods. These anchor points have been used in the self-assembly of these objects in solution to create rod chains, tetrapod networks and propeller-like structures.

Alignment and positioning of these objects onto pre-patterned surfaces, also prepared using self assembly, has been developed extensively and several exciting results have been reached. **The self-assembly of shape controlled nanocrystals mastered by the SA-NANO consortium is well beyond the current state of the art, as reported in the up-to-date scientific literature.** We indicated in the final version of Annex 1 of the project that external biases including electric and magnetic fields, as well as microfluidics, will be used to achieve rod alignment and assembly. **These tasks have been carried out with excellent results.** Theoretical modeling on self-assembly to support the experiments has also been performed. We anticipated that assemblies of shape-controlled nanocrystals will likely reveal new collective phenomena that we were going to study by diverse techniques, including optical spectroscopy, magnetic studies, and scanning probe methods. **We have now uncovered many of these effects**. In addition, we planned to compute electronic and optical properties of isolate and assembled nanocrystals by accurate theoretical methods. Also these tasks have been carried out at a satisfactory level.

In general, most of the milestones and of the deliverables planned at the beginning of the project have been reached.

3. Most important problems during the period including the corrective actions undertaken

No major problems have occurred during the whole duration of the project and therefore no major corrective actions were undertaken.

4. Main achievements of SA-NANO per each Workpackage

Workpackage 0.

Project Management (Leader: National Nanotechnology Lab of CNR-INFM)

Workpackage objectives

The objectives of this workpackage, which deals with the overall management of the project, are to provide an efficient plan for the scientific review and assessment of the project, to provide the administrative, financial and legal management of the project, and to manage and disseminate the generated knowledge.

Task 0.1. Scientific Management

Collaborations, exchange of students and researchers, visits.

In the first year, the two key scientists of HUJ (Uri Banin and Oded Millo) collaborated closely on the spectroscopic studies of nano-dumbbells. They also performed assemblies of nanocrystals, first focusing on InAs dots. Banin and the Tel Aviv group of Prof. Rabani (TAU) worked on the mechanism of one-sided growth of Au on nanorods. The procedure of nano-dumbbell water solubilization was transferred for use by the Lecce group (CNR-INFM) on their NDB system. HUJ transferred nano-dumbbell samples to the Heidelberg group (UHEI).
The group of CNR-INFM (Manna, Krahne) collaborated with the group of Parak (LMU) on the synthesis of CdTe tetrapods, on the selective growth of semiconductor tips on nanorods and on the water solubilization of nanocrystals. Two graduate students from LMU visited CNR-INFM for several months (one student for two months and the other student for four months). Two researchers from CNR-INFM visited LMU for a period of two weeks. At this time, one former PhD student working in the LMU group moved to Lecce (CNR-INFM) with a postdoctoral position.
The group of LCC-CNRS collaborated with CNR-INFM on the growth of Au tips on CdTe tetrapods prepared by CNR-INFM. The two partners tried different chemical precursors to grow Au tips. The group of UHEI cooperated with HUJ and with CNR-INFM on the assembly of Au-tipped nanocrystals on the patterned substrates that UHEI prepared. A PhD student from UHEI visited CNR-INFM for six months.

In the second year, one postdoc from CNR-INFM visited UHEI for two months, one student from LMU for two months, and one staff researcher visited UHEI for some weeks.

In the third year, the exchange of researchers was also significant. In particular, people from CNR-INFM and from LCC-CNRS went to UHEI. People from CNR-INFM and from PC-RAS visited IMAPH in May 2007. Also, there was an intense exchange of samples among the partners. Finally all the partners have been engaged in the preparation of the final SA-NANO conference, which was held in Lecce in May 2008. LCC-CNRS has continued the collaboration with HUJ on the preparation and study of magnetic and optical properties of CdSe-Co hybrid nanocrystals (WP1), and with UHEI on a) the direct growth of nanorods on patterned substrates (WP3) b) assembly of Au-tipped Co nanorods on dithiol functionalized substrates (WP3) and alignment with the aid of a magnetic field (WP4). IMAPH made 2 trips to CNR-INFM (one in 2007, one in 2008) and organized ternary meeting of CNR-INFM, IMAPH and PC-RAS at Minsk in May 2007. Samples developed by CNR-INFM were used by IMAPH for synthesis and further research.

Meetings.

In the first year, at the beginning of SA-NANO (February 4th, 2005), a kick-off meeting was held in Lecce, Italy. It was hosted by CNR-INFM and was attained by all partners. In the tenth month (December 2nd 2005) a Project Coordination Committee meeting was held in Munich (Germany). This “internal” meeting was hosted by the LMU partner and was attained by all the partners.

In the second year, the project reached its half life. Therefore, in September 2006, the mid-term assessment meeting was held in Lecce, Italy. It was hosted by CNR-INFM and was attained by all partners, as well as by the project officer and by the External Advisory Board. The meeting was successful and the final version of the report was accepted by the commission, meaning that the SA-NANO project was positively evaluated and allowed to continue until month 36.

During this last reporting period of SA-NANO, the project reached its conclusion (this last reporting period was 40 months long instead of 36 as we could obtain a 4 months extension). The major event was the organization of the final conference SA-NANO in May 2008 in Rome, which we coupled with the third of a series of European conferences (“NANAX”, nanoscience with nanocrystals), the first of which was organized in Munich in 2003, the second in Grenoble in 2006, and the third was planned to be organized in Lecce. In February 2007 a Project Coordination Committee (PCC) meeting was held in Rome (Italy). This “internal” meeting was hosted by CNR-INFM and was attained by all the partners. We also had a final SA-NANO meeting in Rome on June 19th-20th 2008, in which we discussed the main achievements of the project with respect to the original planning, the actions taken to exploit the project results and disseminate the knowledge, and again also future actions that will be taken by the consortium in this respect, and also the possibility to submit new proposals in the forthcoming FP7 calls.

Reports.

During the first year, an interim activity report at month 6 and a periodic report at month 12 were filed.

During the second year, we filed an interim activity report at month 18, a mid-term assessment report at month 19, and a periodic report at month 24.

During the third reporting period, an interim activity report was filed at month 30. Finally, at the end of the project, the following reports have been delivered: i) The periodic activity report covering this last reporting period from month 25 to month 40; ii) A publishable final activity report (the present one), covering main aspects of the work, objectives, results and conclusions, and the final plan for using and disseminating the knowledge. The final report on the actions taken to engage with the public will be included in the final plan for using and disseminating the knowledge; iii) A final management report for the full duration of the project consolidating the claimed costs of all the contractors in an aggregate form covering the entire duration of the project, including the last reporting period; iv) A final funding distribution report consolidating the funding distributed to each contractor over the entire duration of the project; v) The update of the Project fact sheet.

Task 0.2. Administrative, Financial and Legal Management

The Administrative and financial support functions of SA-NANO have been delegated to a staff of experts affiliated with CNR-IFNM throughout the duration of the project. The financial manager has been operating operate under the budget, accounting and auditing schemes of CNR-INFM, Italy. Additionally, a legal manager already affiliated with CNR-IFNM has handled the consortium agreement.

Major changes to the consortium.

As of *June 1st* 2005, *Consiglio Nazionnle delle Ricerche(CNR)* took over the rights and obligations of *Istituto Nazionale per la Fisica della Materia (INFM).* Any reference in the contract, including Annex I and the table of the estimated breakdown of costs, to *INFM* was deemed to be a reference to *CNR* therefore *Consiglio Nazionale delle Ricerche* became a member of the consortium identified in Article 1.2. Notwithstanding the transfer referred to above, the Commission and/or the Court of Auditors of the European Communities and their authorised representatives continued to enjoy the rights referred to in Article 29 of Annex I1 to the contract in respect of work undertaken by INFM which continued to be bound by all these provisions of the contract and its Annexes relevant to the effective exercise of these rights.

Following the successful evaluation of a proposal that was submitted on May 16th 2006 under a specific call inviting proposals for the addition of partners from Targeted Third Countries (TTC) to running / under-negotiation projects which meet certain conditions, new partners were included in the consortium. These new partners were the “Institute of Molecular and Atomic Physics of the National Academy of Sciences of Belarus” and the “Photochemistry Center of the Russian Academy of Sciences”. An **Addendum 1** (final version filed on December 10th 2006) was therefore prepared, which implemented the Annex 1 of the starting SA-NANO project.

On July I, 2007 the B.I. Stepanov Institute of Physics of the National Academy of Sciences of Belarus has become an official assignee (legal successor) of the Institute of Molecular and Atomic Physics of the National Academy of Sciences of Belarus (IMAPH). The B. I. Stepanov Institute of Physics took the whole scientific, managerial, financial and legal responsibilities for the FP6 projects which were being conducted by the Doctor of Science Sergey Gaponenko and his laboratory. The whole staff of his laboratory and himself have continued the research at the B. I. Stepanov Institute of Physics with every personal contract remaining valid without interruption and equipment staying in the same labs. This change of affiliation has required a change in the SA-NANO contract. Therefore, an amendment request was filed and the change was approved by the Commission.

During the third year of the project, upon submission of an amendment request, the SA-NANO project was extended by additional 4 months. This change was necessary in order to finalize the various activities.

Task 03. Management and dissemination of the generated knowledge

The SA-NANO website

A website was set up by CNR-INFM for the dissemination of knowledge and the exchange of information in between the partners of the project (www.sa-nano.it). The website is currently functioning and accessible. The delivery of the final version of the website has been at the end of the first year, according to what was planned in the project and it was fulfilled. In the web site there are several links. These are: Partners, Project Objectives, Tutorials, Image Gallery, Expected impact, FP6 Program, Publications, Contact us, Useful links, and Reserved Area.

Other dissemination activities.

The partners have been actively engaged in dissemination activities that included: i) Publication of the SA-NANO results in high-impact scientific journals; ii) Communication of project results at national, international conferences and seminars; iii) Divulgation activities such as presentations for the general public, high school visits at the labs, writing of articles to magazines (such as for instance an article for the "Parliament Magazine" on the SA-NANO objectives and achievements).

Management and protection of the generated knowledge

Consultations are now under way among the partners as to whether to file some patent applications. In general, as the present project was more directed at understanding the fundamental aspects of self-assembly in nanocrystals, the work carried out has not lead to issues of IPR protection so far.

Additional details can be found in the final plan for the management and dissemination of the generated knowledge, which we are also delivering.

Workpackage 1.

Development of shape controlled nanocrystals with anchor points for self assembly and functionalization (Leader: Laboratoire de Chimie de Coordination, LCC-CNRS)

Workpackage objectives

The objectives of this workpackage were the synthesis of a new generation of shape- and composition- controlled nanocrystals with specific recognition elements, as well as their surface functionalization. Shape-controlled growth with topological control has been developed. More specifically we have been working on nanorods and tetrapods with metal, semiconductor, and oxide tips that have served as anchor points. The new hybrid nanocrystals have been functionalized with biomolecules for purposes of self assembly.

Task 1.1. Development of nanorods and tetrapods with anchor points for self assembly

CNR-INFM. Metal and semiconductor-tipped nanorods and tetrapods. At the beginning of the project, we have worked together with LMU to refine a method for growing PbSe and CdTe domains on the tips of CdS and CdSe nanocrystals (see later also on the LMU section for this task). During that year we also developed an approach by which CdTe- or PbSe-tipped nanorods could be converted into Au-tipped nanorods. In particular Au was deposited on the rod tips through a selective oxidation process. We also developed a synthesis of titanium dioxide nanorods with cobalt tips

New approaches to highly homogeneous samples of nanorods and tetrapods. For the assembly of superlattices of shape-controlled nanocrystals a high degree of control over the nanocrystal shape was essential. In this respect, CNR-INFM has carried out work along several directions. First of all, it refined during the first and second year, a method for the controlled growth of CdTe tetrapods, based on a synthesis in a mixture of phosphonic acids. During the second and third year we have then developed an approach for the seeded growth synthesis of nanorods made of a seed of CdSe and a shell of CdS, with a ultra-narrow distribution of rod diameters and lengths. This has allowed us to realize assemblies of nanorods on much larger scales than previously reported, and with new revolutionary approaches, see WP4. We have then extended this method to the synthesis of tetrapods of various combinations of materials (II-VI semiconductors) with an excellent control of sample homogeneity. Then we have actively exploited these materials for the creation of the networks of tetrapods, for chains of nanorods and for propeller-shaped assemblies, see WP2. Finally, an additional surprising outcome of this work is was the development of maghemite (Fe_2O_3) tetrapods.

Other heterostructure nanocrystals. We have developed heterodimers of $CoPt_3$ and Au nanocrystals. Although strictly speaking this was a deviation from the planned activity, these dimers can be considered indeed as Au-tipped nanocrystals and therefore important building blocks for the various tasks of SA-NANO. Also, we have developed a synthesis of FePt-iron oxide heterodimers, of rod-shaped TiO_2 brookite nanorods and we could selectively grow iron oxide domains on such nanorods.

HUJ. A new set of hybrid nanoparticles with anchor points for self assembly has been developed throughout the SA-NANO program. Moreover, various new mechanisms important in the growth of such hybrid systems have been unravelled. A first approach involved the use of a semiconductor particle as a template for the growth of a metal. In the start of this program we synthesized Au tipped CdSe nanorods (nanodumbbells), where a simple room temperature reaction leads to Au growth selectively on the rod apexes. For tetrapods, the same reaction leads to Au growth on all four arm apexes. Under increased concentration of Au, a transition from two sided Au growth to one sided Au growth was discovered, and assigned to a mechanism involving electrochemical Ostwald ripening. Experimental and theoretical analysis showed that fluctuations in Au tip size lead to one tip being dissolved while the other grows. This mechanism thereby extends the realm of ripening phenomena and their significance in nanostructure synthesis, in particular for nanocrystals composed of different materials. The asymmetric metal-semiconductor heterostructures thus formed constitute novel nanostructures offering intrinsic asymmetry for one-sided chemical accessibility through the Au tips and for diverse device functionalities. This synthesis approach was later extended to growth of Au on CdS rods. Reacting Au with InAs nanocrystals, however, revealed a new phenomena, in which at room temperature Au diffused into the particles forming a central Au core surrounded by an amorphous shell.

LCC-CNRS. We had experience in the synthesis of several metal, metal oxide and semiconductor nanoparticles, however hetero-structured nanocrystals with a controlled localisation of the constituents had never been prepared in this lab before.

The first task for LCC was the synthesis of metal tipped Co nanorods, which were already available. However, during this project, a new synthetic procedure was developed in order to overcome the practical problems related to the synthesis and sensitivity of the precursor used up to then.

The first metal of choice for Co nanorods was gold. Co is a metal that can be easily oxidized and the galvanic displacement of Co by gold was a side reaction necessary to be avoided. For this, different Au precursors with different oxidising ability were tested. It was found out that the use of $AuCl_3$ as well as AuCltht, resulted in complete dissolution of the Co nanorods, while the more stable $AuClPPh_3$ permitted the growth of gold nanoparticles on the Co nanorod without destroying them. Moreover the possibility of controlling the localisation of the gold on the nanorods was demonstrated. The competition between gold nucleation and ligand exchange on the nanorods surface, offers the possibility to favour one over the other by choosing the reaction conditions. It was therefore possible to control the position of gold, either selectively on the tips of the nanorods or in a non-selective way over the nanorods whole body.

We have synthesized Co tetrapods which could serve in a subsequent step for the development of metal tips as in the case of the nanorods. The low yield of tetrapods obtained did not permit to go further in this direction. However we obtained cobalt multipods in high yields and we have verified that the same principles that govern the growth of gold on cobalt nanorods were applicable in the case of multipods. We have therefore obtained gold tipped and gold decorated multipods.

Finally in collaboration with HUJ we have synthesized cobalt tipped CdSe nanorods. In this case we have obtained two types of objects: i) CdSe nanorods with spherical Co tips; ii) CdSe nanorods with Co nanorods grown at the tips. The magnetic and optical properties have been studied.

LMU. Synthesis of advanced inorganic nanoparticles: LMU and CNR-INFM have worked together to refine a method for growing PbSe domains on the tips of CdS and CdSe nanocrystals. They succeeded in growing PbSe tips on the one or on both sides of semiconductor nanorods. Both partners have also developed a method to grow very small clusters of CdSe. These clusters do not grow continuously, but grow from one configuration to the next bigger stable one. Due to this stepwise growth these particles are also termed magic size clusters.

Task 1.2. Surface functionalization of shape-controlled nanocrystals to make them water soluble

CNR-INFM. At the beginning of the SA-NANO project we had developed, in cooperation with LMU, a polymer coating procedure for transferring different types of nanoparticles into water by means of an amphiphilic polymer. While the approach is robust, cheap and generally applicable, the polymer that was originally employed is unfortunately not commercially available anymore and the bare extension of the original protocol to another amphiphilic polymer is not straightforward. As a result of a search for a polymer with similar structure that could be implemented for such procedure, we developed a new procedure that exploits the commercially available Poly(maleic anhydride-*alt*-1-octadecene) (henceforth referred to as C_{18}-P) on colloidal nanocrystals of different compositions and shapes. We have demonstrated that the original coating procedure needed to be modified substantially in order to be extended successfully to the new polymer. In particular, Furthermore, we developed an ultracentrifugation procedure that makes the entire purification step of the nanocrystals (once they have been coated with the polymer) faster, more efficient and reproducible than the previously reported procedure.

HUJ. To realize the biochemical assembly routes of WP2, we have also developed a methodology for water solubilization of the dumbbells. Optimal conditions to maintain stable dispersion without compromising the Au tip quality were achieved by performing ligand exchange reaction using mercapto-undecanoic acid (MUA), as the water stabilizing agent for dumbbells.

LMU. Polymer-coating procedure for hydrophobic nanoparticles: A polymer coating procedure developed by the Parak group (LMU) in cooperation with the Manna group (CNR-INFM) has been employed to nanocrystals composed of many different materials, including shape controlled objects (CdSe nanorods) and hybrid materials (Au-tipped nanorods). This procedure employs an amphiphilic polymer, and consists of “wrapping” several polymer chains around each nanocrystal, resulting in a polymer shell embodying each nanocrystal. Addition of suitable molecules cross-links the polymer chains around each nanocrystal and stabilizes the polymer shell, ensuring a more robust coating. Polyethylene glycol (PEG) molecules have been attached to the polymer shell, so that the particles repel each other also by steric repulsion. In this way they are much more stable in electrolytic solutions than the ones without the PEG.

Characterization of colloidal properties: The polymer coated nanocrystals were very found to be very stable in aqueous environment. By HPLC and gel electrophoresis the particles were purified from unreacted molecules and from the elution profiles aggregation effects also could be excluded. The stability of the particles in buffer solutions was investigated in detail by fluorescence correlation spectroscopy (similar to dynamic light scattering). These experiments demonstrated that aggregation can be neglected and that the particles are highly stable.

Transfer of rods and dumbbells into aqueous solution: The LMU partner has applied the polymer-coating procedure to Au-tipped semiconductor nanorods. As it turned out the surfactant around these dumbbells directly after synthesis is not very strongly attached to the surface of the dumbbells. Therefore initial attempts to transfer dumbbells to water via polymer coating failed, as the dumbbells precipitated. The LMU partner has solved this issue by first attaching a stronger surfactant to the dumbbells' surfaces: After incubation with mercapto-modified alkyl chains the rods become stable enough for being polymer coated. In this way now dumbbells can be transferred to aqueous solution with two methods: ligand exchange (Banin group, HUJ partner) + polymer coating (Parak group, LMU partner). The water-solubility was investigated with two methods: HPLC and gelelectrophoresis. With HPLC it was also possible to remove unbound excess polymer from the actual polymer-coated dumbbells. With gel electrophoresis the very good water-solubility was demonstrated, as the particles remain soluble even while been squeezed through the pores of the gel under high salt concentration.

Incorporation of functional organic molecules in the polymer shell: LMU has developed a new procedure, in which biological molecules can be directly embedded in the polymer with which hydrophobic nanoparticles can be solubilized in aqueous solution. For this purpose the amphiphilic polymer it synthesized by the LMU partner instead of purchasing it. Hydrophobic side-chains and the biological molecules (such as biotin) are linked to the hydrophilic backbone. The particles are then coated with the complete polymer. In this way no post-conjugation is needed. This has the advantage that unfavorable salt-conditions during post-conjugation can be avoided. In particular we have shown that with this method it is possible to make nanoparticles with exactly one, two, and three biotin-molecules per particle. This method also allows for embedding marker molecules in the polymer-shell of the particles. This can be used to control binding also via fluorescence techniques. Data also indicate that during the polymer-coating procedure excess micelles are generated, which have to be removed with gel-electrophoresis.

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Task 1.3. Targeted surface (bio)functionalization onto tips of nanocrystals developed in tasks 1.1 and 1.2

LMU. Particles with a defined number of binding-sites: LMU has developed a general procedure to link exactly one or exactly two anchoring points per nanocrystal. In order to form linear chains of nanorods in a very controlled way, each rod must possess exactly one anchoring point at each of its ends. Multiple anchoring points could lead to branching. A general procedure has been developed by the Parak group to link exactly one or exactly two anchoring points per particles. Amino-modified PEG has been attached to the -COOH groups of the surface of polymer-coated Au or CdSe/ZnS nanoparticles with standard bioconjugation chemistry using 1-Ethyl-3-(3Dimethylaminopropyl)carbodiimide Hydrochloride (EDC). If NH_2-PEG with a molecular weight > 5000 g/mol is used discrete bands can be observed in gel electrophoresis. We ascribe these bands to particles with no, exactly one, exactly two, etc. PEG molecules attached per particle. In order to introduce functional groups as anchor points for further attachment of biological molecules, PEG molecules with two modified ends were used. Particles modified with NH_2-PEG-NH_2 exhibit free amino groups on their surface so that molecules bearing a N-hydroxysuccinimide ester (NHS) functionality can be directly attached via the formation of a covalent bond. We demonstrated this for the case of NHS-PEG-biotin resulting in biotin-modified particles. In this way we have achieved a big progress concerning the development of nanoscale LEGO blocks. We can functionalize polymer-coated nanoparticles (with inorganic cores of basically every possible material) with an exactly controlled number of anchor groups. So far we have demonstrated -SH, -NH_2, and -biotin anchors. We have also demonstrated that these anchor points are still reactive towards their corresponding ligand molecules.

Investigation of site-specific attachment: Together with the Banin group (HUJ partner) the Parak group (LMU partner) has started to develop an assay with which site-specific surface functionalization can be investigated. The idea is to use small Au particles with site-specific ligands as probe. When such a probe is added to a nano-structure with site-selective attachment points it can only bind to these sites. One example are for example Au-tipped semiconductor rods. When Au-particles with thiol groups are added to this structure they only should be able to bind to the Au, but not to the semiconductor part. With the TEM this site-selective attachment could be visualized in a very intuitive way. First, the LMU group developed probes with only one active ligand, in particular polymer-coated Au particles with just one free SH-group per particle. These particles and control particles with no SH-group were then added to plain big Au nanoparticles. As to be expected the Au probes with the SH-group bind to the Au surface, whereas there is only very little nonspecific attachment of the Au particles without SH-groups.

Task 1.4. Development of methods of synthesis of nanorods including nanorods with anchor points for self assembly based on « water-in-oil» microemulsions

PC-RAS. Development of new methods to grow size and shape controlled nanocrystals of different nature based on «water-in-oil» microemulsions as chemical nano-reactors including metallic, semiconductor and organic nanoparticles.

Monodisperse gold nanoparticles of both spherical and anisotropic shape have been synthesized in TX-100 reverse micelles at low values of W (W = [H_2O]/[detergent]) using different combinations of sodium sulfite and L-ascorbic acid as a reducing agents.

AOT reverse micelles were used for the preparation of CdSe nanoparticles using aqueous solution of $CdSO_4$ and Na_2SeSO_3 as a source of precursors. Nanoparticles of average diameters from 2 to 5 nm were obtained at W = 5 and 10, respectively. Compared to NPs obtained by high-temperature synthesis, the excitonic absorption band and fluorescence spectra are broadened, which is indicative of wider size distribution.

Synthesis of CdS nanoparticles in AOT micelles at W = 10 under ultrasound action leads to formation of rod-like NPs. It is proved by the red shift of the excitonic absorption band and splitting of excitation spectrum into two bands.

Nanoparticles of other different content (AgI, Ag_2S RuS_2, Fe_3O_4 and γ-Fe_2O_3) were also synthesized and investigated in reverse micelles.

Task 1.5. Development of synthesis methods of organic nanocrystals consisting of J- and H-aggregates

PC-RAS. Four methods of synthesis of J- and H-aggregates of cyanine dyes were developed, including the formation of aggregates in a mixture of solvents of different polarity, their preparation in solution in the presence of different additives on surfaces with the following evaporation of the solvent and in the presence of proteins. Presence of polydiallyldimethylammonium results in the formation of several rod-type J-aggregates in acetonitrile. The ability to form J-aggregates on the surface of glass plate, polyethylene terephthalate film and aluminum foil is shown.

Workpackage 2.

Anchor point mediated self assembly of shape controlled nanocrystals in solution (Leader: The Hebrew University at Jerusalem, HUJ)

Workpackage objectives

This workpackage targeted various forms of self-assembly created in solution, using the anchor points as contacts for the assembly.

Task 2.1. The Self Assembly of Nanorods in solution to form chains of type AAAA and type ABAB

HUJ. Formation of various types of nanoparticle chains, linked via the Au anchor points on the hybrid nanoparticles, was realized. Linking with dithiols, such as hexane-dithiol, where the thiol selectively binds to the Au tips, was demonstrated in organic solvents forming AAA type chains in Au-CdSe nano-dumbbells. The control in this case is limited, as addition of large dithiol concentration leads to aggregation. Greatly improved control was achieved by applying a biochemical approach to the linking, employing Avidin-Biotin linking chemistry. Gold-tipped CdSe Rods (nano-dumbbells) were solubilized in an aqueous phase as developed in WP1 and self-assembled in a head-to-tail manner using biotin disulfide and avidin forming AAA type chains. The disulfide end of the biotin molecule attaches to the gold tip of the nano-dumbbell and the biotin end of the molecule is able to conjugate to an avidin protein. The avidin can strongly conjugate up to four biotin molecules. Changing the ratios of biotin to nano-dumbbells lead to the formation of dimers, trimers and flower-like structures. In order to further improve the distribution of chain lengths a separation method based upon weight was applied using a concentration gradient. This clearly demonstrated that the gold tips provide effective anchor points for constructing complex nanorod structures by self-assembly. Mixed ABA and BAB type structures were also achieved, using also avidin-biotin linking. This included assembly of biotinilated NDBs nano-dumbbells (building block A) with Au nanoparticles (building block B) coated by streptavidin.

LMU. Investigation of non-specific binding: Specific self-assembly is only possible if non-specific binding can be excluded. The LMU partner has prepared model systems to investigate the role of non-specific interaction in particle self assembly. We used polymer coated Au nanoparticles with no, and exactly one or exactly two biotin molecules per particle. By combining streptavidin with these conjugates the following interactions can happen. Gold particles without any biotin on their surface should not bind to streptavidin specifically. Gold particles that bind nevertheless can do so only by non-specific adsorption. Gold particles with exactly one biotin per particle can bind specifically to streptavidin. Since ever streptavidin (in unmodified form) has four binding sites for biotin the biggest contract that can result be specific interaction is a streptavidin with four attached Au particles. Au particles with 2 biotins per particle on the other hand can interconnect two streptavidin molecules and thus bigger aggregates can occur. We have investigated this phenomenon with gel electrophoresis. To visualize the streptavidin we used streptavidin-modified quantum dots (CdSe/ZnS). The same amount of streptavidin coated CdSe/ZnS particles was incubated with increasing amount of biotin modified Au particles and the conjugates were investigated with electrophoresis. The CdSe/ZnS particles were visible by their red fluorescence and the Au particles by their red color. In each gel the amount of biotin-modified Au particles per streptavidin coated CdSe/ZnS particle was increased from the right to the left. Free streptavidin coated CdSe/ZnS particles have a very low electrophoretic mobility and move very slowly on the gel. On the other hand, Au particles (with or without biotin) have a much higher electrophoretic mobility. As soon as some Au binds to the CdSe/ZnS the resultant conjugates get a faster mobility than that of plain streptavidin coated CdSe/ZnS. This can be seen in the images: the higher the Au / CdSe/ZnS ratio, the faster the fluorescent bands become. In the ideal case of no non-specific interaction the CdSe/ZnS band should be completely unaffected by the presence of Au without biotin. However, as it is obvious from the first image there is also non-specific adsorption. When Au particles with biotin are used then even smaller amount of Au are sufficient to warrant for increased mobility of the fluorescent band. From these images we can learn that specific biotin-streptavidin mediated binding dominates, but that non-specific adsorption cannot be disregarded. This type of gel assays will be used in the future parts of the project to analyze the role of non-specific interactions in controlled specific self assembly of nanoparticles.

Particle assemblies with sugar- and biotin-based binding sites. LMU has also used the new polymer-coating procedure to synthesize nanoparticles with exactly one biotin per particle. To these mono-functional particles streptavidin was added, so that different biotin / streptavidin ratios were obtained. The results indicate, that the streptavidin-biotin system is not as trivial as often assumed. The formation of linkage between biotinylated nanoparticles and streptavidin critically depends on the streptavidin-to-biotin-ratio. With gel-electrophoresis the binding process was analyzed in detail. Alternatively also sugar molecules were added as binding-sites to the polymer surface of the particles. Selective and reversible binding of these particles could be demonstrated.

CNR-INFM developed a general and simple approach for the assembly in a liquid solution of several shape-controlled semiconductor NCs, such as bullets, rods and tetrapods. We exploited the shape anisotropy of NC to grow small metallic Au domains on selected locations on such NCs. We use then small amounts of molecular iodine (I_2) that destabilize the Au domains and induce the coalescence of Au domains belonging to different NCs, thus forming larger Au particles, each of them bridging two or more NCs through their tips. Such ‘nano-welding’ process leads to linear and cross-linked chain-like assemblies of NRs, to propeller and flower-like structures based on bullet-shaped NCs, and to networks of Tetrapods. The approach is selective towards the Au domains, it takes place at room temperature in a solvent were as-grown NCs are soluble (i.e. toluene or chloroform), and therefore it does not require the use of organic molecules/biomolecules as linkers. The present strategy introduces an inorganic and robust junction between NCs with which the inter-particle distance in the assembled structure is controlled, compared to assemblies mediated by molecular organic linkers that are more flexible. In the case of Au-tipped nanorods their reaction with I_2 led to the formation of nanorod chains that were several tens of NCs long, in which branching points were introduced whenever a Au domain was able to link more than two NR tips

Tasks 2.2. The Self Assembly of tetrapods and rods to create propeller structures

CNR-INFM. The same approach as described in the previous task for CNR-INFM to create chains of rods was followed to grow propeller-like structures. This was somehow a deviation from the original work program, in which we had planned to make propeller-like structures using rods and tetrapods. Instead, we used bullet-shaped NCs. Welding of bullet-shaped NCs, each carrying a single Au domain at the tip of the bullet, led indeed to propeller-like structures. Although such structures tended to stay close to each other on the carbon support film of the grid when the solvent was evaporated, we could identify several of these isolated assemblies. High resolution TEM image of the central part of these propeller-like structure showed that fhe Au region does not grow epitaxially on the CdS surface, since different relative crystallographic orientations between the two domains had been observed in the sample, similar to what was reported by HUJ. Scanning Electron Microscopy tomography sequences of the flower-like assemblies also indicated that these structures are not limited to planar arrangements.

Tasks 2.3. The Self Assembly of tetrapods in solution to form three dimensional structures

CNR-INFM. The same approach as described in the previous task for CNR-INFM to create chains of rods and propeller-like structures out of bullet-shaped NCs was employed to make tetrapod networks. On tetrapods, the welding of Au domains induced the indeed the organization of tetrapods into complex networks that extended for several square microns. It is likely that in solution such assemblies have a 3D globular structure. Their dimensions could be tuned by the amount of iodine added to the NC solution. Also, such assemblies appeared often to be stable in toluene, most likely because they could engulf large amounts of solvent at their interior. Only when an excess of iodine was added to the solution, the size of the networks and the number of NCs entrapped in them increased to an extent that a precipitate was formed.

Workpackage 3.

Self assembly of shape controlled nanocrystals on patterned substrates (Leader: The Ruprecht-Karls-Universität Heidelberg, UHEI)

Workpackage objectives

The objectives of this workpackage are the preparation of substrates patterned with nanocrystal templates of several materials as anchoring points, and assembly of shape-controlled nanocrystals on such substrates. Patterned substrates are being 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 through several recognition mechanisms.

Task 3.1. Controlled self assembly of diblock copolymers at interfaces

UHEI. We used the Poly(styrene-*block*-2-vinylpyridine) (PS-*b*-P2VP) diblock copolymers with different molecular weights. One block (PS) is non-polar while the other (P2VP) is polar. The chemical difference between the two blocks and the different adhesion properties to surface allow for adjusting self-assembly. Spin-coating of the micellar solution together with an annealing process leads to the formation of an hexagonal pattern of clusters with a height of a few nanometers.

Task 3.2. Generation of substrates with patterned anchor points

UHEI. The polar core of the micelles can be loaded with a metal salt. Large surfaces can be covered with a homogeneous, hexagonal pattern of metal particles by dip-coating of the substrates and subsequent plasma treatment. The plasma treatment serves two purposes. First it initiates the reduction of the metal ions and thus the formation of the particles. Second it removes the organic material, i.e. the micelles. By adequate choice of the molecular weight of the polymer, its concentration in solution and the retraction velocity in the dip-coating process the inter-particle distance can be tuned from 40nm to 200nm.

Task 3.3. Self Assembly of rods and tetrapods onto the anchor points prepared in task 3.1

LMU. Synthesis of DNA-Au conjugates with controlled valency for assembly on surfaces: LMU has prepared together with CNR-INFM Au-nanoparticles with a discrete number of oligobucleotides bound per nanoparticle. These conjugates are the building blocks for attachment to oligonucleotide modified Au-surfaces. In particular specific versus non-specific DNA attachment was compared and the size of the conjugates was determined.

CNR-INFM has worked together with UHEI on the organization of nanocrystals, with an without anchoring points to the patterned substrates prepared by UHEI. More specifically, the immobilization of ssDNA, as well as Au-tipped nanorods, $CoPt_3$-Au heterodimers and CdTe tetrapods to one gold-dot was achieved. We performed intensive work in order to identify the correct parameters that control the biofunctionalization of the nanostructured interface that in turn controls ssDNA self-organization under non-denaturizing conditions.

Task 3.4 Surface patterning of semiconductor nanocrystals using di-block copolymer micelles

We have carried out no activity in this directions as results of the first two years of the project have not been promising. We have therefore focused more our attention on other tasks in this WP.

Task 3.5 Transformation into application of optically active hybrid systems

UHEI. Antireflective surfaces are produced with a controlled etching process. For this aim gold nanoparticles are deposited onto fused silica. Reactive ion etching applied to these surfaces leads to the formation of hollow pillars. In this process the individual gold particles focus the reactive ions. This leads to a depletion of ions in the vicinity of the particles and thus the formation of hollow pillars. This surface structuring increases the transmittance of the substrates over a broad spectral range from the deep UV to the IR by 3-5%.

Task 3.6. Templating of shaped semiconductor NC assemblies by means of nanoporous dielectric matrices with regular vertical pores

IMAPH. For the first time we propose and performed experimentally the use of optically transparent dielectric alumina films with regular vertical pores of controllable diameter for spatial alignment of ensembles of semiconductor shaped nanocrystals. The first evidence of the partial CdS nanorods alignment in the porous alumina based on absorption dependence on polarization is provided.

Anodizing of aluminium under certain conditions produces self-organized quasi-regular periodic structures (porous anodic alumina) with hexagonal cells and controlled sizes of the pores from 10 to 400 nm in diameter oriented perpendicularly to the planar surface and up to 200 μm thick. Self-organisation during electrochemical processing gives rise regular pore structures without preliminary templating. This original technology developed at Minsk makes it possible to get regular nanotextured surfaces without expensive and complicate electron-beam lithography.

Semiconductor nanorods developed by L. Manna and co-workers at Lecce have been embedded in nanoporous alumina templates. An extensive spectroscopic study have been made including absorption, luminescence and luminescence kinetics measurements along with luminescence kinetics modeling. It was found that templating of semiconductor nanorods by means of nanoporous alumina with vertically aligned nanometer-size pores results in higher anisotropy of absorption and emission spectra of nanorods and in more complex decay law of luminescence with pronounced development of faster components about 1 ns decay time.

Workpackage 4.

Alignment of nanorods on substrates using self assembly assisted by external biases (Leader: National Nanotechnology Lab of CNR-INFM)

Workpackage objectives

The objective of this workpackage was the realization of aligned assemblies of nanorods. A variety of methods to align nanorods has been developed, including the use of external electric and magnetic fields, and microfluidics. In addition, deposition of rods on patterned surfaces have been combined with the alignment techniques.

Task 4.1. Self assembly of nanorods with and without anchoring tips on substrates mediated by electric and magnetic fields to form aligned arrays

LCC-CNRS. During the nanorod synthesis, extended super-lattices are formed directly in solution. These super-lattices contain nanorods organized the one next to the other along their long axes. Two and three dimensional super-lattices are directly available from the crude reaction mixture. We consider that hydrogen bonding and ionic interactions between the ligands are responsible for this organisation and that the magnetic interactions do not play a dominant role for the formation of these super-crystals. This organisation which is extended over several micrometers does not seem to be improved by application of an external magnetic field.

CNR-INFM has managed to laterally align CdSe@CdS nanorods on micron scale areas. Here we fabricated interdigitated electrode patterns on SiO_2 substrates and applied a bias voltage that resulted in electric fields of the order of 10^5 V/cm. In particular the fabrication of relatively high electrodes (thickness of 0.5 μm) allowed us to achieve laterally aligned nanorod arrays on the micron scale. We also tested two approaches for vertical alignment of nanorods and obtained satisfactory results on a length scale of hundred nanometers. We have measured polarized emission by photoluminescence experiments and anisotropic phonon excitations by Raman spectroscopy on nanorod arrays. The optical characterization also contributes to workpackage 5. We were able to achieve ordered arrays of close-packed, vertically aligned nanorods by drying-mediated self-assembly of the new types of seeded-grown, asymmetric core-shell nanorods, obtained from WP1, on substrates from concentrated nanorods solutions.

As a side issue we explored the possibilities of the assembly of tetrapods in the field of scanning probe microscopy. Tetrapods have the unique property to self align on a flat surface with one arm pointing in the direction perpendicular to the surface plane. We achieved the positioning of single tetrapods on the flattened tip of commercial AFM probes. These tetrapod-functionalized AFM probes were used to image the topography of different samples revealing excellent spatial and vertical resolution.

Task 4.2. Self assembly of aligned nanorods and nanorod chains on substrates using microfluidics.

HUJ. The group studied and developed an effective method for obtaining nanorod arrays with long-range directional order, on a micron-scale range, on a substrate (e.g., Si). This was done by immersing the substrate vertically into a nanorod solution and letting solution-substrate contact line sweep down along the substrate during the evaporation process in a controlled rate. By that, the rods aligned preferentially perpendicular to the contact line, although domains of rods aligned perpendicular to that majority phase were also found.

CNR-INFM achieved a significant improvement concerning the vertical alignment of nanorods mediated by external electric fields leading to ordered arrays of tens of microns size. Together with the already achieved large scale lateral alignment of nanorods this allowed us to study in detail the emission properties of ordered arrays of nanorods. These optical results also contribute to WP5. We have also made considerable progress in the assembly of nanorods mediated by a combination of electric fields and fluidics. We have developed a self assembly approach of colloidal CdSe/CdS core-shell nanorods into laterally oriented arrays by means of the fluid dynamics of drying droplets. In a drying droplet the pinning of the contact line leads to a radial flow of fluid from the center to the edge of the drop in order to compensate for the evaporated liquid at the surface. If the liquid contains nanoparticles this flow leads to a significantly enhanced density of nanoparticles near the contact line, and when the contact line eventually retreats the so called “coffee stains”, i.e. fringes of densely deposited nanocrystals are formed. For a droplet evaporation of a solution of toluene containing CdSe/CdS nanorods we observe the formation of long ribbon structures in which they are aligned side by side within the fringes of the coffee stains, whereas in the central regions we find no specific ordering of the nanorods. The situation changes completely if electrical manipulators with an applied bias voltage are placed onto the supporting substrate within the droplet during the evaporation. The electric potential gradient leads to a vortex like motion of the fluid in addition to the inherent coffee stain fluid dynamics. In this case we find large scale alignment of nanorods in smectic liquid crystal phases within the dense fringes, where the long axis of the nanorods is oriented along the contact line.

Task 4.3. Self assembly of aligned nanorods using a combination of microfluidics and electric fields

CNR-INFM. Rapid linear fluid flow in the channels formed by the interdigitated electrodes described above with the applications of electric fields led to bended, smile-like stripe patterns, where the rods were oriented along the electric field lines in between the electrodes and the smile like structures reflect the velocity profile of the nanorod solution. Performing this experiment on a solvophobic substrate coated with interdigitated electrodes led to an alternating pattern of broad and narrow nanorod stripes on the positively and negatively biased electrodes,

Workpackage 5.

Electronic, optical and magnetic properties of nanorod assemblies and chains (Leader: The Hebrew University at Jerusalem, HUJ)

Workpackage objectives

The objective of this workpackage is the study of the optical, electronic and magnetic properties of shape-controlled nanocrystals (including semiconductor-metal nanodumbbells and hybrid NC systems) and of their assemblies.

Task 5.1. Electronic level structure of nanorods in aligned assemblies

HUJ. We exploited cryogenic scanning tunnelling microscopy (STM) and spectroscopy (STS) in order to obtain spatially resolved information on the local density of states, tunnelling-transport properties and single electron charging effects in nanocrystal (NC) assemblies and hybrid colloidal NCs. In addition, conductive-probe atomic force microscopy (C-AFM) was applied in studies of the intricate electrical conduction and photo-transport mechanisms in semiconductor nanocomposites and 'NC-solids'. These local-probe measurements were performed in conjunction with 'macroscopic' measurements, providing deep insight into the *microscopic* origin of the *global* behavior of such complex systems.

Electronic level structure in nanocrystal arrays and NC-polymer composites: We have found that the band-gap of NCs (dots and rods) within arrays significantly reduces with respect to the corresponding isolated particles. The reduction was found to depend on three main factors: the electron and hole effective masses, and the number of and distance between nearest neighbours. In the densest arrays we have found, surprisingly, an emergence of collective 2D-like electronic level structure [1]. Upon exchanging the 'conventional' capping ligands by π-conjugated linker molecules we have found further reduction of the band-gap [2]. Moreover, by exchanging them by other capping molecules we could rigidly shift the band structure and thus tailor the energetic levels of the NCs to the surrounding matrix, thus improve the efficiency of NC-polymer composite based opto-electronic devices [3].

Determining the band-offset in hybrid semiconductor NCs: Spatially-resolved STS measurements were performed along single seeded-grown CdSe/CdS and ZnSe/CdS QD/NR core/shell NCs. The spectra acquired on the latter system revealed its type-II band-alignment nature, where, in particular, those measured on the core region manifested the type-II gap, between the ZnSe valance-band edge and the CdS conduction-band edge. These results conformed to our expectations. In contrast, the STS results obtained on the CdSe/CdS NCs were surprising. They have shown that both the electron and hole ground states are localized in the CdSe core, in contrast to previous papers which, based on indirect optical data, delocalization of the electron ground-state was reported. The puzzle that arose was that the previously reported CdSe-CdS conduction band-offset, extracted form bulk-like systems, could not support electron localization. To resolve this issue, CNR-INFM (Lecce group) performed energy-level calculations for this system, using the conduction band-offset as a fitting parameter to match the HUJ experimental data. Such band-offset with a reasonable value was indeed found. Importantly, this new combined experiment-theory approach (tested also for the ZnSe/CdS system) was demonstrated to be very effective for extracting band-offsets in hybrid NCs, which may be different from the corresponding bulk systems [4].

Anomalous tunnelling spectra on fullerene-like WS_2 nanoparticles: Current-voltage characteristics measured using STM on fullerene-like WS_2 nanoparticles show zero-bias current and contain segments in which the tunneling current flows opposite to the applied bias voltage. In addition, negative differential conductance peaks appear in these reversed current segments, and the characteristics are hysteric with respect to changing the voltage sweep direction. Such features resemble those appearing in cyclic voltammograms, but were uniquely observed by us in vacuum tunneling. We attribute this behaviour to electrochemical reactions involving the W atoms and water molecules embedded in the sample, processes that are triggered by the large tip-sample voltages applied in our experiments [5].

Task 5.2. Electrical conduction in semiconductor nanorod assemblies

HUJ. *Size dependent local conductance properties of CdSe nanocrystal ensembles:* Local (applying C-AFM) and 'macroscopic' electrical transport measurements performed on CdSe nanocrystals (NCs) assemblies reveal a crossover between two different conduction regimes. The crossover takes place in the range where the average NC radius in the assembly is around the Bohr radius, manifesting the effect of quantum confinement on the electrical conduction properties. Within this work we have developed statistical methods to analyze the current maps measured by CAFM, yielding insight also into the macroscopic conduction properties [6]. Applying a new method developed in our group [7] we are now studying the local dark- vs. photo-transport properties, finding evidence for photo-induced hopping transport and revealing intriguing tip-induced long-range charging effects.

Task 5.3. Anisotropic effects in the optical properties of nanorod arrays and chains.

CNR-INFM. By investigating the photoluminescence of vertically and laterally aligned nanorod arrays we revealed a significant dependence of the emission intensity with respect to the array geometry. Our results led to an optical dipole emission profile of these arrays with strong intensity in the lateral direction and low intensity in the vertical direction. We could also reveal a small dependence of the emission energy with respect to the emission direction. Raman experiments on laterally aligned nanorod arrays showed a slight dependence of the energy of the optical phonon modes with respect to the nanorod orientation.

Task 5.4. Electronic and conduction properties of nanorod chains.

HUJ. *The electronic properties of metal-semiconductor nano-junctions:* By mapping the electronic density of states (at 4.2 K, using STS) along a single CdSe-Au nano-dumbbell (NDB), we provided novel information on the nature of the electrical nano-contact between metallic and semiconducting nanoparticles. In particular, the tunneling spectra reveal, for the first time, the existence of metal induced gap states (MIGS) near the Au-CdSe interface, which decay over a few nanometers towards the centre of the nanorod, consistent qualitatively with theoretical predictions. These states give rise to pronounced negative differential conductance in tunneling spectra acquired on the Au dot near the interface. We have also identified a Schottky barrier effect in this system, although the nanorods length is smaller then the typical extent of the space charge region in metal-semiconductor interfaces [8].

Anomalous photo-voltaic effect in Si-SiO$_2$ NC composites: Local photo-transport measurements (using C-AFM) were performed on Si-SiO$_2$ NC composites, revealing a surprising new photovoltaic effect. Anomalously large photo-voltages of up to 7 V (much larger than the band gap of the Si NCs) developed in samples where the NC-Si concentration was close to (and above) the percolation threshold of the Si NCs network. The built in electrical field developed in the direction of the size (and concentration) gradient of the Si NCs. This effect was attributed to charge separation of excited electron-hole pairs that is governed by the size-dependent quantum confinement and charging energies, and to a cumulative effect of finite-size Si-NC clusters [9].

Task 5.5. Characterization of the magnetic properties of the aligned magnetic nanorods and nanorod chains

LCC-CNRS. The spontaneously formed superlattices of Cobalt nanorods contain also small Cobalt nanoparticles. The magnetic properties of these superlattices are due to these two components. As a result the magnetic properties of the nanorods themselves are masked by the nanoparticles contribution. We have managed to separate the nanorods from the nanoparticles and we have studied the magnetic properties of the pure nanorods. For doing this the spontaneous organisation had to be destroyed. For these unorganised Co nanorods the magnetic switching occurs in one step, and the fast decrease at small negative magnetic fields present in the unpurified sample has completely disappeared. It should be noticed that the remnant magnetization is half of the saturation magnetization. This exactly corresponds to the expected value in the case of a system of nano-objects with a uniaxial anisotropy randomly oriented within the sample. The shape of the hysteresis loops is very near the ideal one which can be calculated in the framework of the Stoner and Wohlfarth theory in the case of an assembly of non interacting uniaxial nanoparticles. The small deviation is due to the presence of a small dipolar interaction field which leads to a small decrease of the coercive field as compared to the non interacting case.

The shape of the hysteresis loop obtained after alignment of the nanorods under a magnetic field, has significantly improved approaching an almost square shape and reaching the value of $0.91M_s$ Furthermore, the coercive field is increased to 6.2 kOe and 10.0 kOe at T = 300 K and T = 2K, respectively. Compared to the values expected by Stoner and Wholfarth predictions, this coercive field is lower. This is due to an imperfect magnetic alignment and since the packing of the nanorods has became dense, dipolar interactions may play a more important role.

The coercive fields we measured in this system of aligned Co nanorods is well above the one generally measured for pure 3d systems. This system free of oxides, as already anticipated from the beginning, is now proved to be a very good candidate for magnetic recording applications.

Task 5.6. Comprehensive analysis of luminescence dynamics of NC assemblies combining advanced experimental techniques (imaging microfluorescence spectroscopy and time-correlated single photon counting) with numerical decay time distribution analysis

IMAPH. Extensive experimental analysis of luminescence properties of semiconductor nanorods embedded in nanoporous alumina matrices with vertically aligned pores has been performed including steady state and time resolved measurements by means of time-correlated single photon counting. Luminescence kinetics of nanorods outside and inside the matrix has been processes by means of the numerical decay time distribution analyses and development of faster components in luminescence decay was found to be inherent for nanorods embedded in matrices.

Task 5.7. Study of absorption and emission spectra of nanocrystals, investigation of their dependence on size and shape of nanocrystals, direct control of the size and shape effect by AFM (Atomic Force Microscopy)

PC-RAS. The possibility to control the size and the shape of nanocrystals as well as their orientation on support depending on the dye concentration, additives, the way of coating and the support properties was shown. The approach was used to prepare J-aggregates of cyanine dyes with defined number of molecules involved in the J-aggregate. It was demonstrated that the number of the binding sites for proteins RNase, lysozyme and trypsin is varied from 6 to 15 and those provides conditions for J-aggregation. J-aggregates were formed for alkyl meso-thiacarbocyanines in the presence of RNase, lysozyme and trypsin. The concentration of J-aggregates for lysozyme is increased with increasing the protein/dye concentration ratio, reaches a plateau and then gradually decreases. J-aggregates are characterized by relatively weak fluorescence, e.g. $\Phi_f = 0.01$ for lysozyme, and by a small Stokes shift of 6-8 nm, indicating almost resonance fluorescence. The formation of J-aggregates correlates with decay of the dimers and is supported by induced CD spectra. J-aggregation proceeds in the range of seconds to minutes with non-sigmoidal kinetics, whereas sigmoidal type kinetic curves were observed only for trypsin

It has been also demonstrated that Ag nanoparticles can be arranged into an organized ensemble using an ordered structure as a template. In this case the plasmon band of spherical nanoparticles splits into two bands typical for elongated Ag particles. This can be associated with the aligning of spherical nanoparticles into linear structures along the flutes of the ordered structure. Such organized ensemble of Ag nanoparticles were also investigated by atomic force microscopy.

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Workpackage 6.

Theory of self assembly and electronic structure calculations (Leader: The Tel Aviv University, TAU)

Workpackage objectives

The objectives of this workpackage are the development of theoretical tools and the modeling of self assembly of shape-controlled nanocrystals. A variety of theoretical tools have been developed to model the self assembly processes of rods and tetrapods. In close contact with the experiments, we have addressed open issues related to the effects of shape, size, anisotropy, solvent and external perturbations (electric fields, microfluidics) on the resulting assemblies. Theoretical calculations have been performed in order to investigate the electronic and the optical properties of isolated and assembled nanocrystals.

Task 6.1. Development of a theoretical approach to model the self assembly processes

TAU has extended the course-grained model for drying-mediated self-assembly of nanocrystals to describe the assembly of various shapes of nanocrystals, with emphasis on the drying-mediated self-assembly of nanorods. To maintain transferability and to provide a model that can describe both the nanorods, solvent and substrate on length and time scales relevant for experiments, we have retained the description of all species and the dynamics to a lattice. Thus, our coarse-grained mesoscopic model contains the necessary features required by the complexity of the self-assembly process of nanorods. The model includes a description of both the solvent and the nanorods on the relevant length-scales, the treatment of translational and rotational diffusion of the nanorods, the treatment of solvent evaporation, and the description of the substrate.

In short, we divide the space into cells, where each cell can contain nanorods, liquid, substrate, or gas. The density of each specie is described by a variable that can take values between 0 (low density) and 1 (high density). A single lattice site is bound by a total density of all species that is ≤ 1. The size of each cell in the lattice equals the typical solvent correlation length. Because the size of a nanorod can exceed the range of correlated solvent fluctuations, they are allowed to span several cells of the lattice. The strength of the interactions between adjacent cells depends on their occupation and on the interfacial area of the nanorod within a given cell. To allow for rotational motion of the nanorods, we take each lattice point with dimensions that are equal to the correlation length of the solvent and divide it to smaller cells. The interactions are calculated on the small lattice with rules that recover the interactions on the large lattice. The rotational and translational motion of the nanorods is carried out on the small lattice. A crucial step in the success of this approach requires that the nanorods have no preferred orientation on the square lattice with and without the solvent. To achieve this we have developed an Monte Carlo procedure such that the shape of the nanorod on the denser grid is slightly modified by choosing two lattice sites that are related by an inversion operation and reversing their lattice values simultaneously to achieve the desired shape and energy.

PC-RAS. The novel model of morphology definition of a structured solid phase is developed at a desiccation of a microdrop or thin film taking into account hydrodynamic flows. Model was used for calculation of morphology of colloidal particles on a glass and polystyrene substrate from a drop of polystyrene nanoparticle solution. The solid phase is formed from the evaporated solution microdroplet on a flat substrate. A radial distribution function of solid phase is a technologically relevant parameter to describe self-assembling of the nanostructures.
The model is successful approbated in interpretation of the experiment with microdrops of colloidal solutions of polystyrene latex particles of 800 nm diameter.

Task 6.2. Theory of Self Assembly of Nanorods and Tetrapods

TAU studied the dynamics of the self-assembly utilizing a stochastic process for the fluctuations of the solvent density and for nanorods spatial and rotational diffusion. We have carried out massive simulations with a parallel cluster computer to study the drying-mediated self-assembly of nanorods, which where compared with the experimental results obtained by the HUJI by CNR-INFM. We have studied the role of solvent evaporation rates, nanorods spatial and rotational diffusion, nanorods coverage, and aspect ratio. Our major conclusion regarding the drop casting experiments is that the orientation correlation length is quite short regardless of whether the nanorods can move fast or slow compared to evaporation, rotate fast or slow compared to evaporation, and regardless of their aspect ratio and coverage. The above result suggests that in order to align nanorods one needs to rely on a different technique (not drop casting) which benefits from the sluggish dynamics during evaporation, i.e. from the fact that for nanorods the drying dynamics do not influence the directional order to a great extent. This will be described in Task 6.4.

Task 6.3. Theoretical modeling of surface roughness and substrate patterning

TAU has also been involved in the development of theoretical modeling of the effects of surface patterning on the drying-mediated assembly of nanoparticles. For example, we have developed a coarse-grained lattice gas model to study the drying-mediated self-assembly of nanoparticles on diblock copolymer substrates. The model describes the nanoparticles, the solvent and the diblock copolymer on length scales that are typical to the solvent bulk correlation length. Monte Carlo simulation techniques were used to delineate the various mechanisms of this out-of-equilibrium hierarchical self-assembly. Several different assembly scenarios corresponding to different selectivity of the nanoparticles/liquid/substrate were discussed. The role of surface tension, evaporation rate, diffusion rate, nanoparticle coverage, and diblock copolymer periodicity was explored. Optimal conditions to form a stripe phase of nanoparticles along with predictions of novel 3D structures resulting from high nanoparticle and solvent selectivity were described.
The first set of simulations was carried out to understand the case where the nanoparticles are strongly attracted only to one block while the liquid interaction with both blocks is identical. We referred to this case as “selective nanoparticles”. Both homogeneous and heterogeneous evaporation scenarios were considered. We have addressed the time evolution of a nonequilibrium initial condition suitable for experiments of thin liquid films. We find that the solvent evaporation occur layer-by-layer. During this time course nanoparticles partially order above one of the domains (stronger interactions) until a dissolution limit is reached. Upon evaporation the nanoparticles order to form a stripe phase where different stripes are super-connected by meniscus-like bridges (also seen experimentally). These bridges serve as paths for the nanoparticles in their course of self-

organization, providing a mechanism that reduces the amounts of defects in the patterned superstructures, and allowing the system to relax to equilibrium. When the system remains fluxional (homogeneous case) the bridges eventually disappear. We find that the partial alignment before the solvent evaporates is crucial for the formation of an ordered stripe phase of nanoparticles. When the solvent screens the interactions between the nanoparticles and the diblock copolymer substrate the nanoparticles accumulate over the screened domains. We have also discussed the effects of changing the periodicity of the diblock copolymer phase and discovered a critical periodic size required to obtain an ordered stripe phase of nanoparticles.

The next set of simulations was carried out for the case of “selective solvent”, where the interactions between the nanoparticles and the different blocks were identical but the solvent interacts differently with the different blocks. We showed that the mechanism for the formation of an ordered stripe phase of nanoparticles is similar to that observed for the “selective nanoparticles” case, where the only difference is that the alignment of nanoparticles is over the B domains since the solvent is attracted more strongly to block A. Here, bridges are formed only when the liquid-diblock copolymer interactions are stronger compared to the nanoparticle-diblock copolymer interactions. After long evolution periods, the bridges eventually disappear, and a small second layer of nanoparticles is formed above the stripes.

Experimentally, it is difficult to control the liquid-substrate and nanoparticle-substrate interactions independently. Therefore, in the last set of results we have studied the combined case of “selective solvent” and “selective nanoparticles”. When the liquid-diblock copolymer interactions are stronger than the nanoparticle-diblock copolymer interactions, a 3D superstructure is formed at low nanoparticle coverage. At higher coverage, the nanoparticles cover completely both blocks. When the liquid-diblock copolymer interactions are weaker than the nanoparticle-diblock copolymer interactions the system forms a stripe phase with small traces of a second layer of nanoparticles. Here, the nanoparticle stripes are somewhat narrower then the width of the A domains due to the fact that the solvent is selective as well and therefore, it covers the sides of nanoparticle domains above the A domains and not above the B domains.

Task 6.4. Theoretical study of the effects of external fields and fluidics on self assembly of Nanorods

TAU. As described above, the drop casting technique failed to provide a route to align the nanorods over micron length scales. Thus, an alternative approach must rely on ordering the nanorods before the solvent has evaporated, while the role of the evaporation dynamics is to bring the rods to a well aligned closely packed superstructure. One such approach is based on the utilizing capillary forces between the nanorods, as recently suggested by HUJI. HUJI’s experiments utilize a new geometry where a wafer is placed in a container with the nanorods impressed inside. As the solvent evaporates, it creates a strong capillary force at the contact line that leads to orientation of the nanorods inside the solvent. Finally, the solvent forms a thin liquid film which dries and leads to ordered arrays of nanorods.

The Rabani group has contributed in several different ways to understand this process. First, we have estimated the different forces that can lead to pre-alignment of the nanorods. We find that the hydrodynamic and electrostatic forces at the air-liquid interface are too weak to align the nanorods, and the only force that is strong enough is the capillary force. For spherical nanoparticles this force is always small, since spherical nanoparticles can minimize this force by changing the degree to which they penetrate the solvent at the air-liquid contact line. However, for nanorods, due to the lack of spherical symmetry, this no longer holds, and the associated energetic can span several to several hundreds of $k_B T$.

To further understand the proposed mechanism, we have carried out massive simulations on our cluster. The first set of simulations was carried for rods with relatively small aspect ratio (3:1) under slow and fast evaporation conditions appropriate for the aforementioned experimental setup. The striking observation is that there is NO orientational order what so ever! This is true for realistic rotational diffusion time independent of the nanorods coverage. In all cases we studied, we start from an initial configuration where the nanorods are orientationally ordered with a random disorder of the center of mass of the nanorods. In addition, the system is completely wet. This initial condition mimics the experimental realization where capillary forces align the nanorods prior to evaporation. We then follow the evaporation kinetics by the aforementioned Monte Carlo dynamics and display the morphologies after the solvent has completely evaporated. The situation is different for larger nanorods. When the nanorods aspect ratio is larger, even when the solvent evaporation is slow, we find that there is a relatively well defined orientation for the nanorods, and alignment can be in the range of several microns. This result is significant and consistent with the experimental observation of HUJI. It also suggests that there is a critical size (or aspect ratio), above this critical size, orientational dynamics are too sluggish to provide a mechanism for angular mixing.

Task 6.5. Development and application of theoretical methods to study isolated nanocrystals

CNR-INFM. We have developed from scratch a Fortran program (named DAVMASS) which can compute the electronic and the optical properties of nanocrystals of arbitrary shapes and dimensions, within the envelop function approximation (single- or multi-band). DAVMASS is highly optimized, uses the Davidson algorithm to diagonalize the Hamiltonian and it is parallel. DAVMASS can also compute (multi-)excitonic effects, self-consistent potential for excited-states, piezoelectric effects and Scanning Tunneling Spectroscopy (STS) profiles.
We have used DAVMASS to model the electronic and the optical properties of:
i) CdTe tetrapods: we found that the electron in localized in the core while the holes are localized in the arms and that observed double-peak in photoluminescence is related to the emission form the second-excitonic level [1].
ii) CdSe/CdS core/shell dot/rod nanocrystals: We could correctly reproduced the absorption spectra [2], which is found to be quite independent from the CdSe/CdS conduction band-offset [3]. We analyzed STS measurements and we found that the CdSe/CdS conduction band-offset in is 0.3 eV [3], in contrast to previous finding. We analyzed high-power photoluminescence experiments and we found that the observed blue-shift is related to a photoinduced screening of the internal piezoelectric field present in the CdSe dot [4];
We have performed an ab initio Density Functional Theory study of the structural and electronic properties of Au/CoPt3 interfaces [5]. We have considered the (111), (001) and (110) facets and we computed the CoPt3 and Au surface energies, Au/CoPt3 interfacial energies as well as adsorption energies of Au atoms on CoPt3. We found that the (110) clean surfaces are most reactive, and the (111) are most stable, and therefore adsorption of gold atoms is more efficient on the (110) alloy facet than on the (111) one. The further growth of gold under strain conditions imposed by the CoPt3 substrate is favored on both (001) and (111) orientations, based on a thermodynamic analysis of interfacial energetics.

Task 6.6. Development and application of theoretical methods to study nanocrystals assemblies

CNR-INFM. We implemented a periodic plane-wave effective-mass cod to investigate the electronic couplings in arbitrary nanocrystals superlattices. We found that the electronic coupling in vertical aligned assemblies of CdSe/CdS nanorods is very small [2] and that the observed blue-shift in photoluminescence is related to the screening of the internal piezoelectric field and not due to exciton-exciton interaction.

IMAPH. Theoretical modeling of electron wave function delocalization in dense quantum dot ensembles for a number of semiconductor compounds: CdSe, ZnSe, CdS, InAs, GaAs. Calculations have been performed using model displacement of 3375 (15^3) spherical potential wells randomly distributed within a fragment of a cubic lattice with a period L. The aim of calculations was to estimate the number of delocalized states as a function of concentration C of nanocrystals, their radius R, and electron effective mass m^*. Following Shklovskii-Efros criterion, a particle state is considered to be delocalized when the energy overlap integral is larger than the difference of energy level shifts in the nearest-neighbor wells because of the influence of all other wells within the system under consideration. Random displacement of wells was described in terms of a deviation of their coordinates with respect to nodes of a regular cubic lattice according to a Gaussian distribution. The results indicate the steady growth of delocalized electron states with increasing concentration of quantum dots. Delocalization more readily occurs for smaller R and m^* values. CdSe and GaAs ensembles show 100% of delocalized states for $R \geq 2$nm at concentrations well beyond close-packing in a simple cubic lattice ($R=2L$). Contrary, InAs dots for R=2 nm show delocalization at close-packed density only. ZnSe dots were found to exhibit delocalization for $R<2$nm only where a particle-in-a-box model based on the effective mass approximation should be used with great care.

To summarize, our modeling showed readily development of electron delocalized states (an analog of Anderson transition in solids) for dense random ensembles of identical quantum dots for materials with smaller electron effective mass (CdSe, GaAs) with radii about 2 nm or less, that is affordable in many experimental situations for which effective mass theory and particle-in-a-box model are still reasonable and justified. For materials with larger mass (ZnSe, InAs) delocalization was found to occur at extreme concentrations (close-packing) for dot radii about 1nm where applicability of the effective mass theory becomes questionable.

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