

NaNaX 4 – 4th Event of the International Conference Series “Nanoscience with Nanocrystals”

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From April 11–15, 2010, more than 120 scientists from 16 countries met for the NaNaX 4 conference at the Evangelische Akademie Tutzing, close to Munich (Figure 1). The conference series NaNaX provides a unique forum for experts in the field of “Nanoscience with Nanocrystals”. It focuses on the synthesis, study, and application of colloidal semiconductor nanocrystals and metal and magnetic nanoparticles. Thirteen renowned scientists from Europe, the United States, Asia, and Australia gave invited lectures, and *ca.* 40 contributed talks and 80 posters were presented. The 2010 meeting was organized by Jochen Feldmann (Ludwig-Maximilians-Universität Munich), Andrey Rogach (City University of Hong Kong), and Peter Reiss (CEA Grenoble, France) (Figure 2), with the assistance of the Cluster of Excellence “Nanosystems Initiative Munich” (NIM).

Synthesis and Assembly. Better understanding of the underlying reaction mechanisms is the basis for the rational development of synthetic strategies for nanoparticles. In his opening talk, P. Mulvaney from the Univer-

ABSTRACT The conference “NaNaX 4 — Nanoscience with Nanocrystals” held near Munich (April 11–15, 2010) brought together a wide range of scientists discussing the most important current issues in the field of colloidal nanoparticles. Chemical synthesis gives access to nanocrystals of controlled size, shape, composition, and surface functionalization. Past research mainly concentrated on cadmium and lead chalcogenide nanocrystals as well as on gold and iron oxide nanoparticles. Today, there is a trend toward the development of nanoscale heterostructures, which combine different classes of materials and exhibit unique optical, magnetic, and electronic properties. Beside their interest for fundamental science, colloidal nanoparticles hold great promise for a wide range of applications. To this end, speakers and poster presenters showed routes for designing and using nanocrystals in biological imaging and sensing, in energy-related applications, and in catalysis. This report gives a nonexhaustive overview of selected “hot topics” in nanoparticle research discussed at NaNaX 4.

sity of Melbourne showed experimental and theoretical studies of the growth mechanisms of CdSe nanocrystals. He demonstrated that, in typical hot injection reactions, nanocrystal growth proceeds under reaction-limited kinetics and that, at early stages, nucleation, growth, and coarsening occur simultaneously.¹ Obviously, nanocrystals’ surface ligands play a key role in nucleation and growth. However, in some cases, the packing of surface ligands can even induce the formation of novel types



Figure 1. Conference venue of NaNaX 4 at Tutzing, near Munich. Image courtesy of Birgit Gebauer.

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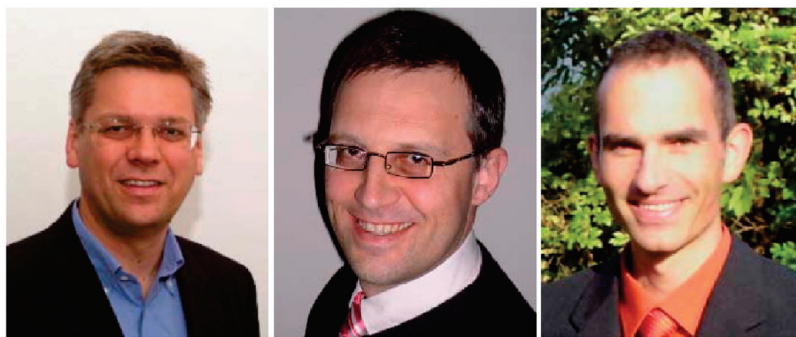


Figure 2. Organizers of NaNaX 4: Jochen Feldmann (Ludwig-Maximilians-Universität Munich), Andrey Rogach (City University of Hong Kong), and Peter Reiss (CEA Grenoble, France). Images courtesy of the organizers.

of low-dimensional structures. H. Weller from the University of Hamburg showed the transformation of 2–3 nm PbS nanocrystals into two-dimensional nanosheets with a thickness of one nanocrystal monolayer. The formation of these 2D structures occurs *via* oriented attachment of individual PbS nanocrystals. The driving force is the lowering of the free energy of the system by forming a dense layer of oleic acid ligands, without interpenetration of the alkyl chains in adjacent layers. Quantitative information on the ligand coverage and exchange dynamics of oleic-acid-capped nanocrystals was obtained by the group of Z. Hens at Ghent University by using a combination of NMR techniques (1D ^1H , ^1H – ^{13}C HSQC, DOSY, and NOESY).² In the case of CdSe nanocrystals, the density of oleic acid molecules on the surface is $3.5\text{--}4\text{ nm}^{-2}$ and addition of excess oleic acid leads to exchange between free and bound ligands with a rate constant of 1 s^{-1} .

Better understanding of the underlying reaction mechanisms is the basis for the rational development of synthetic strategies for nanoparticles.

Although cadmium and lead chalcogenide nanocrystals have been studied most intensively in the past

two decades, research in nanoparticle synthesis is shifting increasingly toward novel materials and nanoscale heterostructures. An illustrative example is the growth of gold domains on semiconductor nanocrystals. On the one hand, a gold shell would facilitate the conjugation of biomolecules on the nanocrystal surface and enhance their biocompatibility.³ On the other hand, the gold surface plasmon resonance strongly influences the optical properties of semiconductor quantum dots, leading either to fluorescence quenching or enhancement. The growth of gold tips on cadmium chalcogenide nanorods, pioneered by the Banin group at the Hebrew University of Jerusalem, aims at improving their electrical contact with electrodes and at exploiting novel self-assembly or photocatalytic properties.⁴ Although it is possible to switch from two-sided (“dumbbell”) to one-sided (“matchstick”) growth by means of an intraparticle electrochemical Ostwald ripening process, this method does not allow increasing the size of the gold domains obtained beyond 3–4 nm in diameter. Larger gold tips would be needed for the thorough study of plasmon–exciton interactions. This problem was recently solved by using UV irradiation during Au tip growth. Upon photoexcitation of CdSe/CdS nanorods, electron transfer to the Au(III) precursor induces the reduction of the latter and formation of 10–15 nm gold tips on one end.⁵ Growing a cobalt tip on the same type of CdSe/CdS core/shell nanorods results in heterostructures that combine fluorescence

with—in view of the small diameter of the Co tip—unexpected ferromagnetic behavior at room temperature.⁶ Synthetic progress in the field of magnetic nanoparticles aims at more complex structures and functionality, as for example in the cases of exchange-coupled Co-tipped Fe_2O_3 tetrapods or cysteine-functionalized $L1_0$ FePt nanoparticles.^{7,8} Carrying out the synthesis of CoPt nanocrystals in the presence of carbon nanotubes can lead to well-defined organic/inorganic heterostructures (Figure 3). After homogeneous nucleation, the nanoparticles attach to the nanotubes due to attractive forces occurring upon charge transfer between the two materials. The nanoparticles can be detached by adding an excess of oleylamine, and the same method can be applied for other types of Pt alloy nanoparticles.⁹

The large-scale assembly of nanocrystals into superlattices and the control of the interparticle distances and surface chemistry are key steps for obtaining solid-state materials of tunable electronic properties, paving the way for their use in (opto-)electronics. M. I. Bodnarchuk from the University of Chicago obtained square inch assemblies consisting of islands of perfectly ordered nanoparticle superstructures with correlation lengths up to 380 nm. These assemblies were prepared by means of thin-film deposition of spherical or cubic 10–20 nm $\text{Fe}_x\text{O}/\text{CoFe}_2\text{O}_4$ core/shell nanoparticles using the doctor-blade technique.¹⁰ In the case of binary superlattices, the temperature of solvent evaporation was shown to be the main parameter for tuning the packing symmetry. With thicker films, monodisperse spherical nanoparticles tend to form mesoscopic void structures and cracks during solvent evaporation, which are studied in the Pileni group at University P. et M. Curie, Paris.¹¹ Converging experimental and theoretical studies showed that the areas of directional and isotropic cracks scale linearly with film height over 3 orders of magnitude. The assembly of *anisotropic* nanoparticles presents additional challenges as compared with superlattices of spherical particles, in which the orientation of

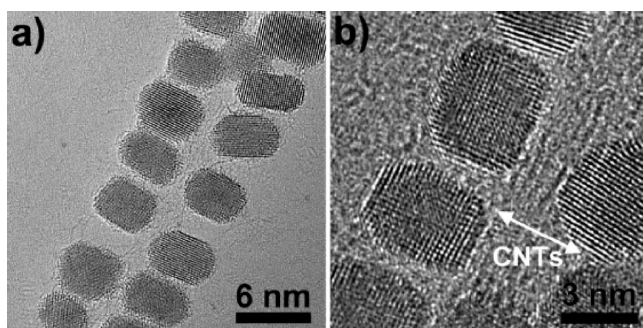


Figure 3. HRTEM image of CoPt nanoparticles, reversibly attached to single-wall carbon nanotubes (CNTs). Reproduced with permission from ref 9. Copyright 2010 American Chemical Society.

each individual nanocrystal does not play a role. In the case of semiconductor nanorods, for example, vertical alignment with respect to the substrate is one of the key steps toward their integration in photovoltaic devices and displays. One method for achieving vertical alignment is the addition of oleic acid to a dispersion of CdSe/CdS nanorods in toluene, which induces the formation of depletion attractive forces. The latter lead to the aggregation of nanorods in sheets of hexagonally close-packed arrays, which can be manipulated in solution and deposited on substrates.¹²

Optical and Electronic Properties. Deeper insight into the photophysical and electronic properties of Cd and Pb chalcogenide nanocrystals and of Au nanoparticles was achieved by applying advanced microscopy and spectroscopy techniques. P. Liljeroth from the University of Utrecht studied coupling in assemblies of quantum dots by means of scanning tunneling microscopy (STM) and spectroscopy (STS). Electronic coupling was observed in the case of PbSe, whereas the spectra of CdSe nanocrystals revealed well-resolved polaron states arising from electron–phonon coupling.¹³ The latter can be investigated by Raman scattering, which also gives information on the nanocrystal shape. In the case of CdSe nanorods, U. Woggon from TU Berlin showed that the position of the longitudinal optical phonon band is purely diameter-dependent, whereas the surface optical phonon band shifts with the nanorod’s aspect ratio.¹⁴ As expected, the growth of ZnS or CdZnS shells on the surface of CdSe nanorods strongly reduces the exciton–phonon

coupling strength. G. Bacher from University Duisburg-Essen studied a different kind of exciton coupling, namely, that of the photogenerated carriers in CdSe nanocrystals with the magnetic spins of Mn²⁺ dopant ions. In these colloidal diluted magnetic semiconductors (DMS), the signature of optically induced magnetization was observed up to room temperature, opening the way for their use in spintronics and spin-photonics technologies.¹⁵

Single-particle spectroscopy has revealed several intriguing properties of

nanoparticles, including, for example, the fluorescence intermittency (“blinking”) of semiconductor quantum dots. The blinking phenomenon reduces the efficiency of quantum dots in LEDs, displays, and lasers and limits their applicability in single-molecule biological tracking and as sources of single photons. Recently, blinking could be strongly reduced or even suppressed by carefully engineering core/shell systems, such as for CdTe nanocrystals overgrown with graded CdTe_xSe_{1-x} shells (Figure 4).¹⁶ However, the origin and mechanism of the blinking process is still under debate. The widely accepted “charging model” says that (i) nanocrystals are in the non-emitting off-state after becoming charged, that is, having a charge carrier delocalized in a nanocrystal electronic state; and (ii) this additional carrier efficiently quenches subsequently photogenerated electron–hole pairs through Auger recombination. M. G. Bawendi from MIT raised doubts about this model. His group found that the photoluminescence quantum yield of the off-state could be 10 times less

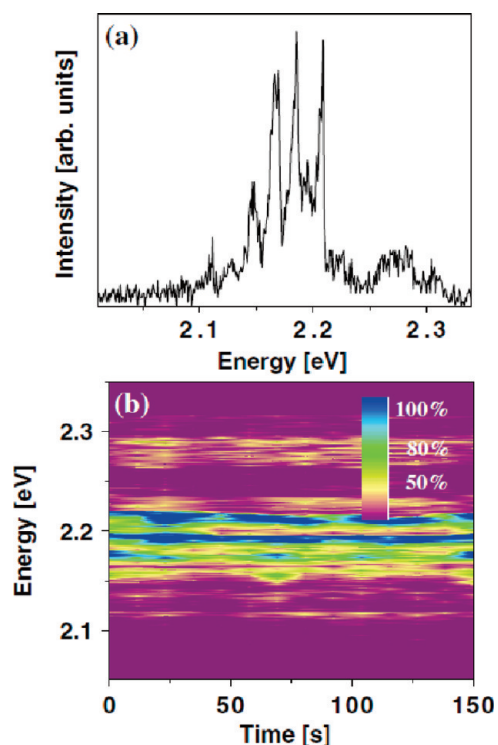


Figure 4. (a) Microphotoluminescence spectrum of a single CdTe/CdTe_xSe_{1-x} nanocrystal, recorded at 4.2 K under illumination with a cw laser of 2.41 eV excitation energy. (b) Contour plot of the PL intensity (inset) versus emission energy and accumulation time. The intensity of the higher energy bands fluctuates by less than 10%, revealing nearly blinking-free behavior. Reproduced with permission from ref 16. Copyright 2009 American Physical Society.

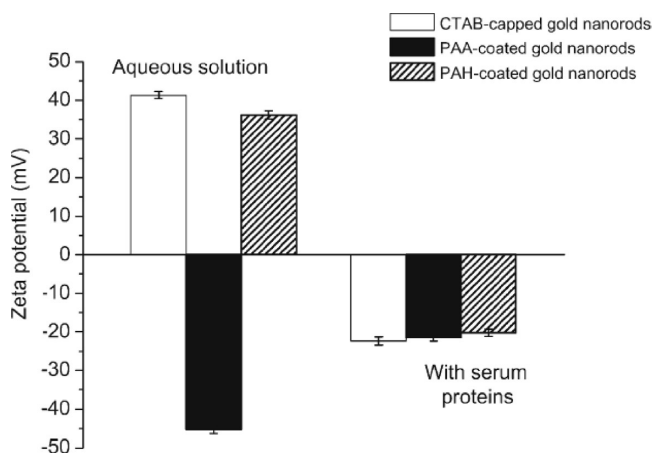


Figure 5. Effective surface charge (ζ -potential) of approximately 12 nm \times 40 nm Au nanorods capped with initial cetyltrimethylammonium bromide (CTAB), negatively charged poly(acrylic acid) (PAA), or positively charged poly(allylamine)hydrochloride (PAH), in the absence (left) or presence (right) of serum proteins. Reproduced with permission from ref 20. Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA.

than that of the biexcitation in CdSe/CdZnS core/shell nanocrystals.¹⁷ However, the charging model predicts that the off-state cannot have a lower emission quantum yield than the biexciton state. Such studies of the single-particle emission statistics generally require nanocrystals with strong and stable photoluminescence. In contrast, V. Sandoghdar from ETH Zürich demonstrated that interferometric microscopy and spectroscopy can be used for the investigation of single nanocrystals even in the absence of fluorescence.¹⁸ Thus, this technique opens the way for photophysical studies of nano-objects emitting with low efficiency. Another fundamental problem concerns the determination of the single-particle emission line width. M. G. Bawendi showed that this value could be extracted from an ensemble emission spectrum by analyzing correlations among the stochastic intensity fluctuations. A Michelson interferometer was used to turn spectral correlations in the ensemble spectrum into intensity correlations recorded by means of fluorescence correlation spectroscopy on a Hanbury Brown–Twiss setup.¹⁹

Biological Applications of Nanoparticles.

The most intensively studied application of colloidal nanocrystals and nanoparticles is likely their use in biological labeling, sensing, imaging, separation, and drug delivery. Understanding and controlling the complex surface chemistry of nanoparticles in biological envi-

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ronments is of paramount importance in this domain. Gold and silver nanorods are very attractive for numerous biological sensing and imaging applications because of their strong plasmon bands whose light absorption and scattering properties can be tuned by changing the nanoparticles’ shape. C. J. Murphy from the University of Illinois at Urbana—Champaign demonstrated the modified interaction of these nanoparticles with living systems after physisorption of various biomolecules (Figure 5).²⁰ Regardless of the original surface charge of gold nanorods, they absorb serum proteins contained in growth media and adopt their physicochemical characteristics (e.g., the

ζ -potential of bovine serum albumin (BSA) of -20 mV). Therefore, surface charge cannot simply be taken as a predictor of nanoparticles’ cellular uptake and cytotoxicity, but nanoparticle–protein interactions have to be taken into account. The local environment also plays an important role in nanoparticle-based ion and pH sensing. By analyzing the response of a pH-sensitive fluorophore as a function of its precisely controlled distance from the surface of gold nanoparticles, W. J. Parak from Philipps University Marburg demonstrated that surface charge strongly impacts the ion binding.²¹ Therefore, the different ion concentrations in the close vicinity of the nanoparticle surface and in the bulk have to be accounted for in the design and readout of ion or pH sensors. H. Mattoussi from Florida State University presented novel conjugates of quantum dots (donors) self-assembled with fluorescent proteins (acceptors) for the realization of fluorescence resonance energy transfer (FRET)-based probes.²² Current research also aims at better understanding the interactions of nanoparticles with living cells. J. Y. Ying from the Institute of Bioengineering and Nanotechnology in Singapore showed that cellular uptake and cytotoxicity of CdSe/ZnS nanocrystals strongly depend on their charge and the hydrophobicity of their surface ligands.²³ A poly(ethylene glycol) coating provided both efficient cell penetration and reduced toxicity. What is happening to the nanoparticles after internalization by living cells? R. Lévy from the University of Liverpool gave one answer to this question: the enzyme Cathepsin L degrades proteins and peptides attached to gold nanoparticles within the endosomal/lysosomal compartments of a wide range of mammalian cells.²⁴

In the field of biological imaging, multimodality approaches have become an attractive strategy for *in vivo* studies with the goal of overcoming the drawbacks of each individual imaging technique. Magnetic resonance imaging (MRI), for example, provides high anatomic resolution and imaging depth but suffers from comparably low detection sensitivity, usually too low for mo-

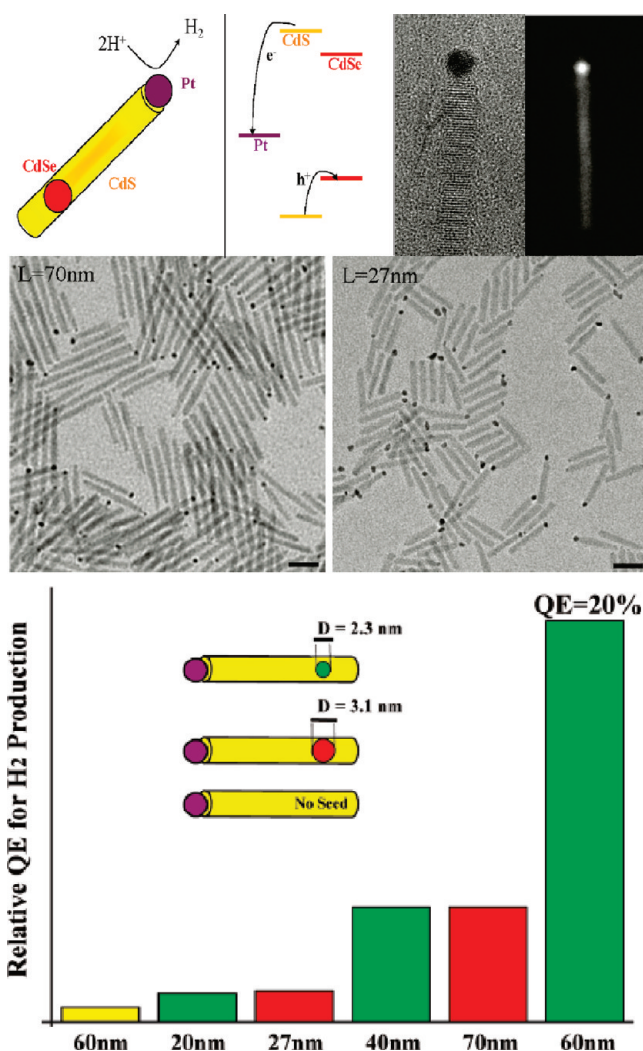


Figure 6. Top: Photocatalytic hydrogen production with 27 or 70 nm Pt-tipped CdS nanorods containing a CdSe seed. Middle: TEM images of the nanocrystals used. Bottom: Relative quantum efficiency for hydrogen production as a function of the dimensions and composition of the nanoheterostructures. Reproduced with permission from ref 26. Copyright 2010 American Chemical Society.

lecular imaging. In this domain, M. Y. Gao from the Chinese Academy of Sciences in Beijing presented the synthesis of superparamagnetic iron oxide nanoparticles by thermal decomposition in strongly polar solvents. The particles obtained have several advantages over commercial contrast agents for MRI in terms of size tunability, monodispersity, phase purity, and the possibility of surface engineering.²⁵ Fluorescence reflectance imaging (FRI) provides much higher sensitivity than MRI, but the imaging depth is generally limited to few millimeters. The near-infrared spectral range is most appropriate for FRI due to reduced light absorption/diffusion and autofluorescence of the biological environment. F. W. B. van

Leeuwen from Netherlands Cancer Institute used the long-lived near-infrared defect state emission of InP/ZnS quantum dots for *in vivo* imaging of sentinel lymph nodes with enhanced signal-to-noise ratios. In addition, visible assessment was possible due to the excitonic orange emission of the quantum dots. However, although iron oxide nanoparticles have been applied at preclinical and clinical stages for more than 10 years, the use of fluorescent quantum dots for *in vivo* imaging of humans is far from becoming a reality and will more likely find applications in small animal imaging.

Emerging Applications. Finally, NaNaX 4 was also the occasion to discuss emerging applications of nanocrystals and

nanoparticles, in particular, in the fields of energy conversion and catalysis. A. P. Alivisatos from the University of California, Berkeley, presented materials for solar fuel generation and, more precisely, for photocatalytic hydrogen generation from water by means of Pt-tipped CdSe/CdS nanorods. Interestingly, the quantum efficiency for hydrogen production strongly depends on the diameter of the CdSe seed and the length of the CdS shell, with a maximum obtained quantum yield of 20% (Figure 6).²⁶ Furthermore, the loss of the Pt tip was identified to be the stability-limiting factor when CdS nanorods without CdSe seeds were used. The latter is supposed to localize photogenerated holes and to keep them away from the sensitive CdS–Pt interface. Nanoparticle *shape* is the key parameter for getting high catalytic activity for ethanol oxidation. In direct ethanol fuel cells, platinum-based catalysts are used for this step, but incomplete and slow ethanol oxidation is currently one of the performance-limiting factors. S.-G. Sun from Xiamen University demonstrated the synthesis of Pt and Pd nanoparticles with open surface structures, that is, containing a high density of low coordination number surface atoms.²⁷ The electrocatalytic activity of these carbon-black-supported nanoparticles is at least two times higher than that of commercial Pt/C catalysts.

In the field of solar power conversion, extension beyond photovoltaics toward thermoelectric devices was dis-

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cussed. Nanoparticles are promising candidates for pushing the thermoelectric figure of merit (ZT) to higher values than those obtained with bulk semiconductors. In nanoparticles, the thermal conductivity is reduced due to phonon scattering, while at the same time the Seebeck coefficient (S) is expected to increase due to quantum confinement. M. Kovalenko from the Talapin group at the University of Chicago presented an original approach for obtaining nanostructured $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ and $\text{PbTe}-\text{Sb}_2\text{Te}_3$ materials with promising thermoelectric properties.²⁸ The approach is based on the use of recently developed inorganic surface ligands consisting of Zintl-type metal chalcogenide complexes (MCCs), obtained by dissolving Sb_2Te_3 in hydrazine.²⁹ The MCCs are used to exchange the organic surface ligands of Bi_2S_3 , PbS , or PbTe nanocrystals, yielding all-inorganic nanocrystal inks, which are suitable for thin-film processing from solution. Upon thermal annealing, the desired alloy materials are obtained, which exhibit high Seebeck coefficients and ZT values up to 0.7.

OUTLOOK

During the last two decades, research on nanocrystals and nanoparticles has developed into one of the major fields in modern science. The discoveries of fascinating optical, electronic, magnetic, and catalytic properties are strongly correlated to advances in chemical synthesis. NaNaX 4 witnessed the preparation of novel nanoscale heterostructures, the development of powerful assembly strategies, and remarkable progress in the understanding of surface ligand chemistry. Together with the development of advanced spectroscopic and microscopic techniques, these results give exciting prospects for the future of the field and pave the way for several practical applications of nanocrystals. NaNaX started out as a small workshop at Ludwig-Maximilians-Universität Munich in Autumn 2003. Followed by the meetings in France (Grenoble-Autrans, 2006) and Italy (Lecce, 2008), the conference has become one of the most important international events on nanocrystals. We

look forward to welcoming you to NaNaX 5 in Spain in 2012. For further information, visit the conference Web site (<http://www.nanax4.de>).

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