Synthesis, properties and perspectives of hybrid nanocrystal structures

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Current efforts and success of nanoscale science and technology are related to the fabrication of functional materials and devices in which the individual units and their spatial arrangement are engineered down to the nanometer level. One promising way of achieving this goal is by assembling colloidal inorganic nanocrystals as the novel building blocks of matter. This trend has been stimulated by significant advances in the wet-chemical syntheses of robust and easily processable nanocrystals in a wide range of sizes and shapes. The increase in the degree of structural complexity of solution-grown nanostructures appears to be one of the natural directions towards which nanoscience will increasingly orient. Recently, several groups have indeed devised innovative syntheses of nanocrystals through which they have been able to group inorganic materials with different properties in the same particle. These approaches are paving the way to the development of nanosized objects able to perform multiple technological tasks. In this *critical review* (165 references), we will summarize the recent advances in the synthesis of colloidal nanocrystals, with emphasis on the strategies followed for the fabrication of nano-heterostructures, as well as on their properties and the perspectives in this field.

Introduction

Colloidal nanocrystals (NCs) are inorganic particles made of a few hundred up to a few thousand atoms, which are synthesized in solution. They can be grown from many different materials and can be cheaply produced in fairly large amounts and with a high homogeneity in size and shape.[1–4] The ability of tailoring the dimensional regime of NCs represents a landmark achievement in materials science, since at the nanoscale both size and shape dictate the peculiar chemical–physical (such as optical, electrical and catalytic) properties of materials.[5–12] Because of their intrinsic robustness and their potential ease of integration with existing technologies, NCs have been intensively developed during the last decades and applications in diverse technological fields are currently under investigation.[13–17] In the synthesis of colloidal NCs, several experimental conditions come into play in the manipulation of their size and morphology, such as the choice of suitable precursors, catalysts, templates, and stabilizer molecules that control their growth, the adjustment of their relative concentration ratio in the liquid phase, and temperature modulation.[18–24] Spheres, cubes,[25–27] rods,[12,28–33]

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stars,[34,35] disks,[36–38] wires,[27,39–42] multi-branches,[27,42–48] and other unusually shaped objects can now be prepared for a variety of materials on the gram-scale with relatively inexpensive equipment. Even more complex NCs are being synthesized nowadays, which are made of two or more inorganic materials combined together.[49–63] In the so-called core/shell NCs, for instance, an additional inorganic material is uniformly grown around a nanocrystal core, for disparate purposes. It can be used to increase the robustness and the fluorescence efficiency of a semiconductor core,[49–53] to tune the magnetic properties of the overall particle,[54,64] and also to provide a surface to which molecules can attach easily.[55] More elaborate approaches, which have been reported recently, can lead to NCs with a finer topological control of their composition. One example is the nanocrystal heterodimer, in which two domains of different materials (for instance, a magnetic one and a fluorescent one,[61] or two metal sections,[62] and so on) are joined together through a specific facet. Another example is the dumbbell-shaped nanocrystal, made of a semiconductor nanorod and one or two domains of another material (such as a metal like Au, or a semiconductor) grown either on one or both tips of the nanorod.[56–58] Other recently reported prototypes of elaborate nanostructures grown by chemists are linear and branched NCs with sections made of different semiconductors,[65] or oligomers of several spherical domains (of different materials) attached to each other in a way that resembles the spatial organization of atoms that form simple molecules.[59,60] This review will focus on such novel types of NCs made of multiple inorganic materials joined together without the need of organic linkers, herein referred to as "hybrid NCs", and will highlight the synthetic strategies which lead to their formation. Also, the chemical–physical properties of hybrid NCs and their perspectives in nanoscience will be emphasized.

It appears clear that such a novel generation of hybrid NCs could represent a revolutionary approach to nanoscale building blocks. As an example, while luminescence nanoparticles have been exploited for bio-detection and bio-sensing[16,66–68] and magnetic nanoparticles for targeted drug delivery,[69,70] magnetic bio-separation[71] and detection,[72] the combination of fluorescence and magnetism into a single nanoprobe would be naturally more advantageous. Efforts have been devoted indeed to develop nanocomposite materials which comprise organic fluorescent molecules (which however are often prone to photo-oxidation) and NCs, embedded for instance in silica capsules,[73,74] or magnetic NCs attached to fluorescent NCs by means of ligand molecules.[71] A more convenient approach to a multifunctional probe would be the preparation of hybrid nanostructures directly by colloidal syntheses, through which each nanocrystal could be, in principle, made of any desired inorganic materials purposely assembled together for tailored applications. Importantly, the latter approaches should enable control of the topology of the resulting nanostructure, while guaranteeing that each of its components retains the same properties as those in the isolated material.

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Liberato Manna received his MSc in Chemistry from the University of Bari (Italy) in 1996 and his PhD in Chemical Sciences from the same university in 2001, discussing a thesis on the use of organic templates to control the size and shape of colloidal nanocrystals. During his PhD studies, and later as a postdoctoral fellow, he worked at the University of California, Berkeley (USA). Since 2003 he has been a postdoctoral fellow at the National Nanotechnology Laboratory of CNR-INFM in Lecce (Italy) where he is responsible for the Nanochemistry division. His research interests are the development of new synthetic approaches to colloidal nanocrystals, the study of their structure, as well as their assembly.

Hybrid NCs based on semiconductor materials would be useful for optoelectronic and photovoltaic applications. Adjacent domains of semiconductors having different band gaps and appropriately chosen band offsets could either trap electron–hole pairs in specific regions of the NCs, thus forcing them to recombine therein with high efficiency, or separate electrons from holes.[65] Useful applications could emerge also in the field of catalysis, as nanocrystal sections of certain metals combined with metal oxides could allow the photogenerated charge carriers to perform redox reactions with high efficiency.[75–78] Therefore, the potential for biomedical, optoelectronic, photocatalytic, and various other applications will be expected to scale dramatically with an increase in the complexity of NCs that can be fabricated. We will discuss in more detail all these possible scenarios in the following sections.

As the concepts for growing hybrid NCs represent a further implementation of those developed for morphological control of nanoparticles, this paper will first give an overview of the various solution approaches developed for size and shape control of NCs. The reader will find it easier then to grasp the various strategies reported so far that lead to hybrid NCs.

Size and shape control of colloidal NCs

In this section, we will outline briefly the most popular solution methods to synthesize NCs which aim to control their size and their shape. For an in-depth coverage of this field, the reader can refer to several reviews.[2,4,11,21,24] More specifically, herein we will show how these methods can be implemented for the purpose of fabricating more complex NCs, in which different materials are combined at the nanoscale. In these latter cases, additional parameters come into play, such as interfacial strain, interface energy, surface reactivity, and crystal solubility.

In the past, several methods have been explored to produce colloidal particles with uniform sizes and size distributions. Many of these pioneering methods relied on a simple principle: the presence, in the system, of a reservoir of reactive molecular species, called "monomers", that contributed to the material growth. It was established that a nearly constant supply of monomers over time[79] allowed for a facile control over size, while keeping the dispersion of sizes relatively narrow. Unfortunately, the diameters of such particles were commonly of the order of hundreds of nanometers, far larger than the realm of sizes that are of interest for nanoscience (which are usually in the range of 10 nm or less). Obviously, the control over size and size distribution becomes a more challenging problem in such dimensional regimes. In the synthesis of colloidal NCs, the key strategy stands within the use of specific molecules, which act as terminating or stabilizing agents, ensuring slow growth rate, preventing inter-particle agglomeration, and conferring stability and further processability to the resulting NCs.[2,4] Often, such molecules are chosen among various classes of surfactants. Surfactants are molecules composed of a polar head group and one or more hydrocarbon chains with hydrophobic character. The ones commonly used in colloidal syntheses include alkyl thiols, amines, carboxylic and phosphonic acids, phosphines, phosphine oxides, phosphates, phosphonates, and various coordinating solvents (*e.g.* ethers).

As of today, refined approaches have been developed for the synthesis of NCs, based on different techniques. In one of the most successful approaches, the so-called "hot injection" method (see a recent review[23] on the topic), the growing medium is a liquid mixture of surfactants and the whole synthesis process is usually carried out at high temperatures under an inert atmosphere. In general, the molecular precursor species are introduced into the growing medium *via* a fast injection. In some cases, however, it is more suitable to mix the reagents at low temperatures and then to slowly heat the resulting mixture up to a target temperature.[1] The decomposition of the precursor species induces a short burst of nucleation, that is subsequently followed by growth of the initially formed seeds. During the synthesis, the surfactants play a key role in tuning the reactivity of the monomers, and in regulating the temporal evolution of the nanocrystal size over time in a controlled way, as they are continuously adsorbing and desorbing from the surface of the NCs through their polar head groups. The combination of specific surfactants and of high temperatures facilitates the formation of NCs with narrower size distributions, with fewer internal defects and with a more uniform surface reconstruction, hence having well defined physical properties (for instance, strong plasmon absorption or luminescence in a relatively narrow interval of energies from metal and semiconductor materials, respectively). When the synthesis is stopped by lowering the reaction temperature, a surfactant coating layer around the NCs remains tightly bound to their surface and guarantees their full solubility in a variety of solvents.

Relatively monodisperse colloidal NCs of a wide range of materials can be easily synthesized by means of several approaches, all based on the above general synthetic scheme. Frequently, NCs synthesized as described above evolve into roughly spherical or faceted shapes. Faceting arises as certain facets have lower surface energy and/or lower growth rate than others, and therefore tend to develop a larger surface area.[80] The type of crystal habit in a nanocrystal can be governed by the particular types of molecules used to control their growth, as they can have different binding affinities to the various facets and therefore influence their surface energy and growth rate significantly.[81–84]

The growth of NCs with anisotropic shapes (wires, rods, discs, branched shapes and so on) can be achieved with several techniques. As of today, the most commonly followed approaches for preparing variously shaped NCs in solution are the use of templating media (membrane nano-pores,[85–90] micelles[20,22,91,92]), growth in the presence of a catalyst,[31,42,93–95] growth by oriented attachment,[47,96–99] the use of surfactants or more generally of solvents that induce or enhance anisotropy,[18,19,25,32,34–36,39,100] synthesis in the presence of external biases, such as electric or magnetic fields,[101–103] and seeded growth.[12,46,104–107] Fig. 1 shows a few selected examples of variously shaped colloidal NCs of different materials. We will briefly review here each of these approaches.

Growth in templating media

There are many examples of nanorods and nanowires of various materials grown in templating media. As examples, nanowires of several metals and semiconductors have been produced *via* electrochemical deposition in porous membranes[85–90] (Scheme 1, panel 1). Polymer (*e.g.* polycarbonate) membranes or porous anodic aluminium oxide are often used, although the latter is preferred, due to the high regularity in

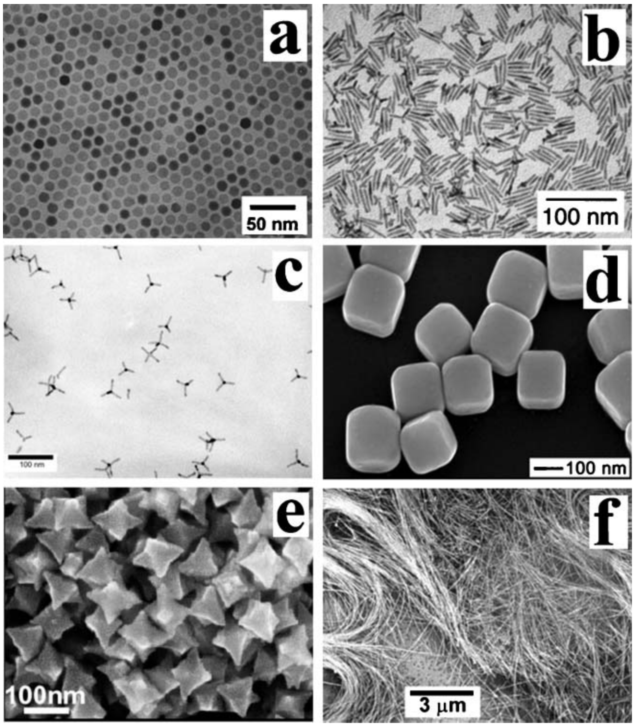
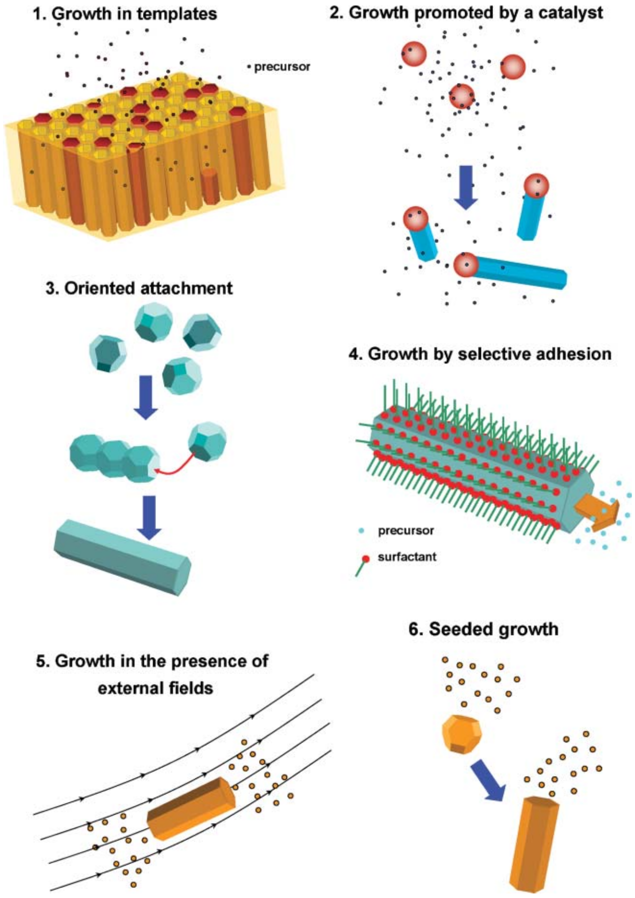


Fig. 1 Examples of colloidal NCs grown with different shapes: (a–c) TEM images of γ-Fe_2O_3 nanospheres (a, reprinted with permission from ref. 106. Copyright (2001) American Chemical Society), CdSe nanorods (b, reprinted with permission from ref. 29. Copyright (2000) American Chemical Society), and of CdTe tetrapods (c); (d–e) SEM images of Ag nanocubes (d, adapted from ref. 25), PbS stars (e, reprinted with permission from ref. 35. Copyright (2006) Wiley), and of PbSe nanowires (f, reprinted with permission from ref. 97. Copyright (2005) American Chemical Society).



Scheme 1 Established approaches to grow NCs with anisotropic shapes.

pore sizes. Rod, wire and platelet shaped NCs have been prepared also by confined reactions in micelles.[20,22,91,92] Micelles are self-organized nanoscopic structures that form, for instance, when water and a non-polar solvent are mixed in the presence of amphiphilic molecules (such as lipids, surfactants, some polymers and also some proteins). Various parameters, such as the temperature, the relative abundance of the water and of the 'oil' solvent, as well as the type and concentration of the amphiphilic molecules, regulate the way in which these latter pack together and form self-assembled micelles with different sizes and shapes. Chemical reactions can be carried out controllably inside such self-aggregated structures, which can be regarded as ''nano-reactors'', that yield NCs whose shapes resemble those of the micelles themselves.

Growth in the presence of a catalyst

The vapor–liquid–solid (VLS) growth mechanism in which a solid rod-like nanocrystal grows out of a catalyst particle on a substrate has been exploited in the growth of one-dimensional nanostructures[108–112] and has been recently translated into the solution growth of colloidal nanorods and nanowires of several materials (Scheme 1, panel 2).[31,42,93–95,113] In the latter so-called solution–liquid–solid (SLS) approach, the catalyst is a colloidal metal nanoparticle that is either injected into the solution together with the precursor molecules needed to grow the desired NCs, or is nucleated *in situ*. Each of these catalyst nanoparticles promotes unidirectional growth of NCs directly in solution. Demonstrated examples are nanorods/nanowires of CdSe, InAs, InP, Si and Ge, some of them synthesized under supercritical conditions.[31,42,93–95,113] So far, it is not fully understood yet whether the catalyst particle (which should be in an almost molten state) becomes supersaturated with the precursor atoms, which then precipitate out forming a wire, or whether it simply offers a preferential site for the decomposition of the precursor molecules, followed by a rapid diffusion of the monomers along the surface of the catalyst particle, at which they coalesce and ultimately generate a wire. Branched nanostructures can also be produced by the SLS approach, as in the case of branched CdSe nanowires.[42] Growth of PbSe rods, cubes, stars and multi-pods in the presence of noble metal particles has been demonstrated recently.[107] However, the conditions of growth allowed one to exclude the occurrence of a SLS mechanism in this system, pointing rather to a heterogeneous nucleation of PbSe on the existing metal catalyst seeds.

In principle, the SLS approach yields ''hybrid'' nanocrystalline materials (*i.e.* InP nanorods with an Au domain on one tip[31,114]), although the quality of these NCs is still low in terms of distribution of rod lengths and diameters, and in addition doping of the rod section with catalyst atoms cannot be excluded.

Oriented attachment mechanism

In this mechanism,[47,96–99] nearly isotropic NCs are first formed in solution, followed by their fusion along some preferential crystallographic directions, leading often to wires,[96] rings,[97] rods,[98] and branched NCs[47] (Scheme 1, panel 3). Although the driving force for this type of mechanism is still unclear, one possible explanation is that the coalescence of nanoparticles along certain directions might reduce the overall surface energy by eliminating some high-energy facets. This process may be facilitated when the organic ligand shell is partially removed from the surface of the initial NC seeds or when weakly coordinating molecules are used as NC stabilizers, so that dipole–dipole inter-particle interactions are enhanced and one-directional NC attachment is spontaneously promoted. One advantage of this method is that even materials that crystallize in highly symmetric structures (*i.e.* PbSe in the rock-salt structure[97] or ZnS in the zinc-blende structure[98]) can be grown in the form of anisotropic NCs.

Surfactant or solvent directed anisotropic growth

For certain materials, there can be found surfactant molecules that are able to passivate the various facets of the NCs with different bonding strengths, thus enhancing or depressing their relative growth rates[18,19,25,32,35,36] (Scheme 1, panel 4). The NCs, in the presence of such molecules (which are prone to selective adhesion) and of high concentrations of precursors, can evolve into strongly anisotropic shapes, as they elongate along those crystallographic directions which grow the fastest. For this mechanism to be operative, however, the NCs have to crystallize in phases that possess a unique axis of symmetry (examples are the hexagonal close packed structure for Co,[36] the wurtzite structure for CdSe,[29] CdS and in some cases for ZnSe,[115] the hematite structure in Fe_2O_3,[116] the anatase structure for TiO_2[82,117]), which will be either the fast or the slow direction of growth, thus yielding nanorods or nano-discs and platelets, respectively. It is important to remark that anisotropic growth of NCs occurs under kinetic control, *i.e.* when the system is overdriven by a high concentration of monomers.[118] Under these conditions, the most unstable facets (those passivated less efficiently), will grow faster. At low concentration of monomers, the growth is more under thermodynamic control, and the situation will be reversed. Atoms will start detaching from the most unstable facets and will feed other facets. Over time the overall habit of the crystals evolves toward the shape that minimizes the overall surface energy. There are reported cases, however, in which the anisotropic crystal structure is not a key requirement in order to grow shape-controlled NCs. PbS NCs, for instance, which crystallize in the highly symmetric rock salt phase, could be grown in shapes ranging from rods to multipods, stars and cubic shapes, depending on parameters such as the growth temperature and the concentration of monomers.[34] While also in this case the surfactant can play a role in modulating the growth rate of the various facets, kinetic factors are likely to be more relevant. Indeed, several solvothermal routes have been reported so far which yielded anisotropic shapes for a variety of crystals that are formed in highly symmetric structures, with no unique axis of symmetry (such as for instance cubic sphalerite, rock salt or spinel structures).[34,39,100] In most cases, a "solvent templating" mechanism is invoked, which involves the formation of complexes between the solvent molecules and the ions that will be engulfed into the crystal.[34] These complexes help to achieve a local structuring along some preferred directions, therefore promoting anisotropic crystal growth.

Anisotropic growth induced by external biases

In the case of magnetic materials, which possess easy magnetization axes, the growth in the presence of magnetic fields can induce anisotropy, leading in a few cases to the formation of nanowires elongated in the easy magnetization axis direction[119,120] (Scheme 1, panel 5). In most cases, in fact, the presence of magnetic fields promotes only the piling up of NCs to form ordered arrays of particles along the field directions.[101,102,121] Nanowires have been produced also in the presence of electric fields.[103] One potential advantage of these approaches is that one-dimensional NCs can be produced at the locations where they are needed, for instance, between two electrodes, as the anisotropic growth direction is often the one along a field line.

Seeded growth

Especially in the case of noble metals (Ag, Au, Pt), unidirectional NC growth can be easily achieved by a seed-mediated reaction mechanism[12,46,104,105] (Scheme 1, panel 6). In this approach, nearly spherical NCs (the "seeds") of well-defined size are prepared and subsequently mixed with a metal salt precursor and with a mild reductant in the presence of suitable surfactants. The seeds act as efficient redox catalysts for metal ion reduction, which occurs selectively at their surface, as the energetic barrier for heterogeneous nucleation is much lower than that for homogeneous nucleation. As a consequence, fast monomer addition to the seeds is guaranteed under assistance of facet-selective surfactant adsorption, which promotes anisotropic growth into nanorods, nanowires and also branched nanostructures.[46] This method has been also extended to the size and shape control of other materials.[106]

Motivation to grow hybrid NCs

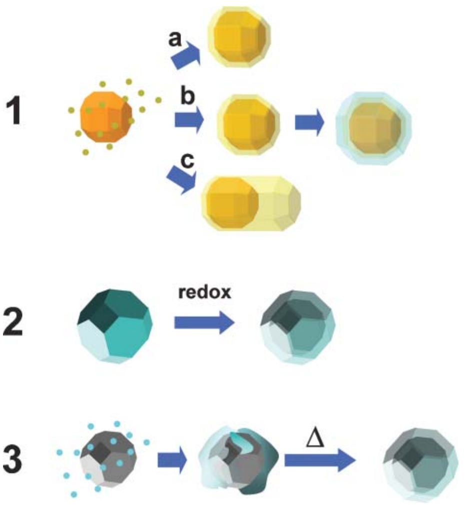
In many of the bottom-up approaches envisaged by nanotechnology it would prove advantageous to have nanostructured materials in which the various units, each characterized by peculiar physical properties, surface chemistry and morphology, could be combined together into a single nano-object, as highlighted in the introduction. In the realm of nanostructures there are already several examples of architectures based on inorganic materials, such as self-assembled quantum dots on suitable substrates,[122] multiple quantum wells and nanowires made of sections of different materials (also called nanowire superlattices, usually grown by the VLS approach),[111,112,123] or multi-layered nanowires.[90,124] Nanowires with stripes of different materials have been grown also by templated electrodeposition, through sequential reduction of different types of ions in the pores of mesoporous membranes.[86,89,125] In these structures, an increasing degree of complexity, and therefore of functionality, is being achieved, as multiple materials are linked together in a programmed way.[126] As an example, the compositional variation in striped metal nanowires offers the possibility of selectively functionalising the various regions within the same nanowire with different molecules, for purposes that can range from the assembly of such functionalized nanowires to biological multiplexing.[125]

With similar aims, colloidal techniques are trying to develop elegant extensions of the synthetic routes to NCs described above. These involve the fabrication of "hybrid NCs" in which domains made of different materials can be assembled together in a unique nano-object. These nanostructures would merge the properties of the individual materials, with new properties being likely to arise from their combination.

Synthesis of hybrid, core–shell NCs

In the synthesis of NCs made of more than one material, the formation of a large interface between the two materials is frequently observed when the lattice constants of the two components do not differ significantly or when the control of synthesis parameters allows the interfacial energy to be kept low. These prerequisites lead to the formation of core–shell type hybrid NCs, in which the symmetry of the inner nanocrystal core is retained upon coverage by a layer of another material, ultimately yielding an onion-like structure. The related preparation techniques usually aim to obtain selective heterogeneous nucleation of the shell onto preformed NC cores while suppressing formation of separate NCs of the second material. The key strategy to achieve this relies on performing a rather slow addition of the shell molecular precursors to the cores at relatively low temperatures. Shell growth can be accomplished by several methods, such as: (i) by co-reacting all the necessary molecular precursors[127,128] or by alternating deposition of monolayers of each atomic species that will compose the shell material[129] (Scheme 2, paths 1a–c); (ii) by replacement redox processes, in which the outermost layer of the core is sacrificially converted into the shell material upon reaction with suitable reagents[130–133] (Scheme 2, path 2); (iii) by thermally-induced annealing of an initially amorphous and/or discontinuous shell[134] or by phase segregation of a starting material alloy[135] (Scheme 2, path 3). As various mechanisms can be involved in shell growth, several combinations of metal, semiconductor, magnetic and oxide materials have been successfully combined, leading to heterostructures that do not necessarily involve epitaxy between the inorganic components.

So far, core–shell-type NCs have been realized for disparate purposes. The cases reported most often are related to fluorescent semiconductor NCs. Established examples comprise associations of various semiconductors (such as CdSe, CdS, CdTe, ZnS, ZnSe) in which the outer shell of a higher band gap material increases the robustness and enhances the photoluminescence (PL) quantum yield of the core[49–52] (Scheme 2, path 1a). One possible configuration is the one in which the band alignment at the heterojunction of the two materials is such that the energy levels of both the valence and the conduction band edges of the core material are located in the band gap of the shell material (such a band alignment is called ''nested'', or type I). This makes both carriers strongly confined to the core material, enhancing the probability of their radiative recombination, as in the well-known highly fluorescent CdSe@ZnS[49,50] and CdSe@CdS[51] NCs. Differently, when only one of the band edges of the core material is located in the gap of the shell material (such a band alignment is called ''staggered'', or type II), the photogenerated carriers are likely to be separated at the core–shell interface. This allows, for example, the PL emission of CdTe@CdSe NCs to be red-shifted considerably up to the near-IR region, as radiative recombination can arise from carriers localized across the core–shell interfacial region.[136,137] This case represents a clear demonstration of a novel property arising in hybrid NCs which cannot be achieved by their isolated components (*e.g.* IR emission from a nanocrystal made of a high-band gap material).



Scheme 2 Sketch of possible mechanisms leading to core–shell nanocrystal heterostructures: growth of a single, of a multiple or of an asymmetric shell on nanocrystal cores (paths **1a–c**, respectively); shell formation following a redox replacement reaction with the initial core (path **2**); formation of a uniform shell upon thermal annealing of an initially amorphous and/or discontinuous coating (path **3**).

In more elaborate approaches, sequential growth of multiple shells is performed for various purposes (Scheme 2, path 1b). If an intermediate shell is buried between a core and an outer shell, it can help to reduce the strain arising from differences in lattice parameters between the two materials. In fact, the shell cannot usually grow thicker than a few monolayers without developing structural defects (such as misfit dislocations) which are detrimental to PL emission.[49–52] For example, in CdSe@MX@ZnS NCs[138] (where MX = CdS or ZnSe), introduction of a MX buffer layer improves the PL efficiency and the photo-stability of the system significantly over that of conventional CdSe@ZnS NCs (Fig. 2). This strategy has been followed also to coat CdSe cores of various shapes, such as nanorods, where growth of a CdS–ZnS shell of graded or mixed composition allows strain to be released gradually.[139] Other examples include, for instance, the fabrication of prototype quantum confined structures such as the quantum dot–quantum well system, in which a layer of a small band gap material is sandwiched between a spherical core and an outer shell, both made of a higher band gap material, and such that at both heterojunctions there is a type I band alignment.[140] In this case, carriers are confined in this intermediate layer and recombine radiatively from this region. This represents somehow a ''quantum shell''.

Although the shell growth usually proceeds in a centrosymmetric manner with the respect to the starting cores (*i.e.* a uniformly thick shell is grown around the original nanocrystal), exceptions may be created by suitable manipulation of the involved reaction kinetics. This has been demonstrated, for instance, by the formation of a rod-shaped CdS shell on CdSe spherical NCs (Scheme 2, path 1c), which confers on them relevant optoelectronic properties (*e.g.* large Stokes shifts and linearly polarized emission) which are inherent of one-dimensional systems.[141]

Several other combinations of materials have been developed which often exhibit unprecedented properties as compared to those offered by their corresponding isolated counterparts. The effect of shell deposition on the resulting optical properties is even more dramatic in noble metal core–shell NCs, which exhibit remarkably modified surface plasmon absorption bands, as compared to those of the starting seeds.[63,132,133,142] Providing a magnetically active core (*e.g.* Fe, Co) with a Pt or Au shell *via* a transmetalation reaction (Scheme 2, path 2) allows for an efficient modulation of its response between the superparamagnetic and the ferromagnetic states,[143,144] while simultaneously offering a suitable surface to which biomolecules can attach more easily.[55,145,146]

Another interesting type of core–shell nanostructure is the Co@CdSe. The growth of a CdSe shell on Co NCs led to

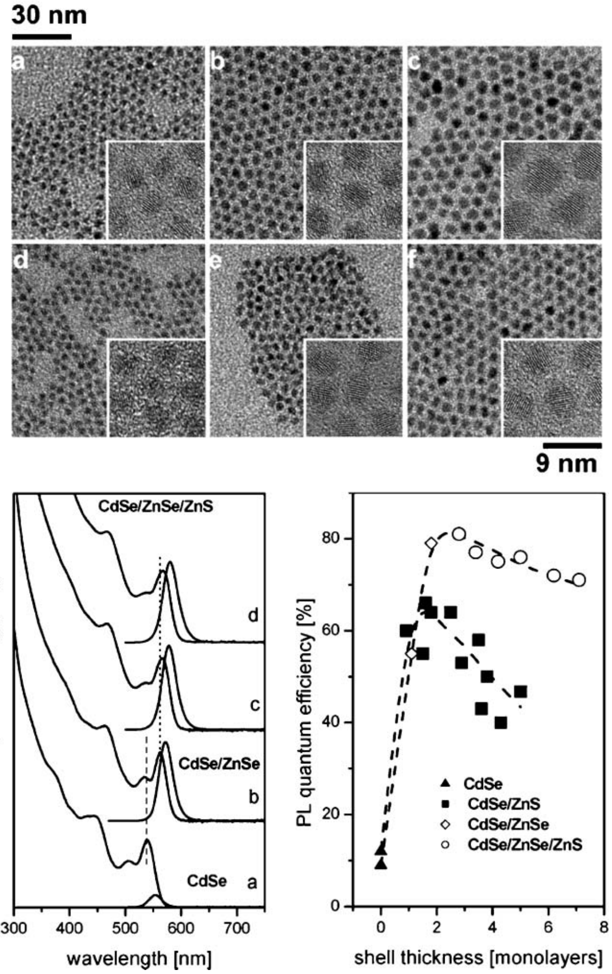


Fig. 2 Top: TEM and HRTEM images of (**a**) CdSe, (**b**) CdSe/CdS, and (**c**) CdSe/CdS/ZnS NCs prepared by consecutively growing CdS and ZnS shells around the same CdSe cores. TEM and HRTEM images of (**d**) CdSe, (**e**) CdSe/ZnSe, and (**f**) CdSe/ZnSe/ZnS NCs prepared by consecutively growing ZnSe and ZnS shells around the same CdSe cores (reprinted with permission from ref. 138. Copyright (2004) American Chemical Society). Bottom: Left: absorption and PL spectra of (**a**) CdSe cores, (**b**) CdSe/ZnSe core–shells (thickness of ZnSe shell $\sim$2 monolayers), (**c**, **d**) CdSe/ZnSe/ZnS NCs with a ZnS shell thickness of $\sim$2 monolayers (**c**) and $\sim$4 monolayers (**d**). Right: room-temperature PL quantum yields of CdSe, CdSe/ZnSe, and CdSe/ZnSe/ZnS NCs dissolved in chloroform. For comparison, the dependence of PL quantum yield on the shell thickness for various samples of CdSe/ZnS NCs is shown (reprinted with permission from ref. 138. Copyright (2004) American Chemical Society).

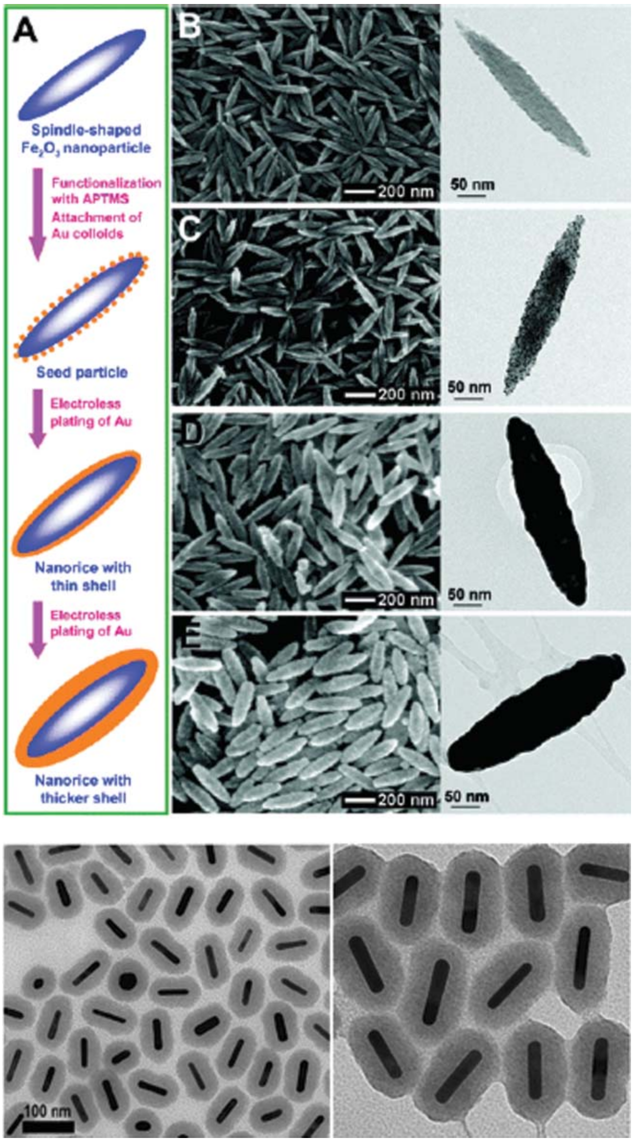


Fig. 3 Top: (**A**) Schematics of the fabrication of hematite@Au core-shell nanorice particles. SEM (left) and TEM (right) images of (**B**) hematite core (longitudinal diameter of 340 ± 20 nm, and transverse diameter of 54 ± 4 nm), (**C**) seed particles, (**D**) nanorice particles with thin shells (13.1 ± 1.1 nm), and (**E**) nanorice particles with thick shells (27.5 ± 1.7 nm) (reprinted with permission from ref. 149. Copyright (2006) American Chemical Society). Bottom: TEM images of Au@SiO_2 core–shell nanorods (reprinted with permission from ref. 155. Copyright (2006) American Chemical Society).

fluorescent nanoparticles, and in addition the NCs showed a reduced blocking temperature, which is a unique characteristic of this material association.[134] In general shell growth on magnetic nanoparticles has an influence on their magnetic behavior. The magnetic properties of iron oxide@Au[64,147–149] and FePt@Fe_3O_4 NCs[54] can be modified for instance by tuning the shell thickness, as this affects the exchange coupling between the two materials and/or among interacting particles (Fig. 3, top panels A–E).

Metallic deposits on oxide NCs (TiO_2, ZnO) greatly enhance the photocatalytic and photoelectrochemical responses of semiconductor cores, as photoinduced charge carrier separation is promoted upon electron migration toward the metal domain. The latter can also favor fast electron release to suitable acceptors in the solution.[75–78] Encapsulation of nanosized noble metal NCs with a SiO_2 or TiO_2 shell (Fig. 3, bottom panel) has been used to alter their surface plasmon oscillations in a controlled manner and to provide light-stable nanoreactors with intact catalytic activity and/or with interesting electron-storing ability.[150–155] The silica coating procedure, on the other hand, has been extended to several classes of materials, including semiconductors, which become stabilized against photochemical degradation while still retaining their fluorescence.[156] The formation of a SiO_2 shell requires an

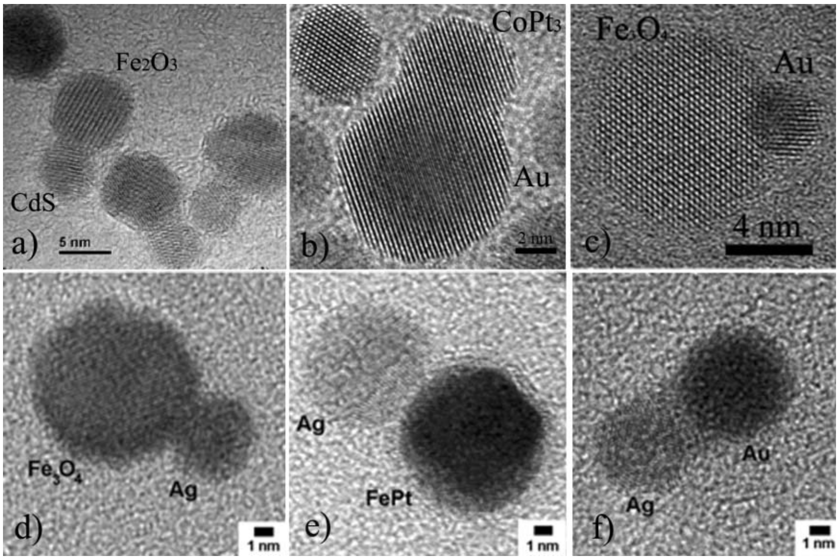


Fig. 4 High resolution TEM images of different types of heterodimers: (**a**) γ-Fe_2O_3–CdS (adapted with permission from ref. 59. Copyright (2005) American Chemical Society); (**b**) $CoPt_3$–Au; (**c**) Fe_3O_4–Au (adapted with permission from ref. 162. Copyright (2006) American Chemical Society); (**d**) Fe_3O_4–Ag (adapted with permission from ref. 61. Copyright (2004) American Chemical Society); (**e**) FePt–Ag (adapted with permission from ref. 8. Copyright (2002) American Physical Society); (**f**) Au–Ag (adapted with permission from ref. 61. Copyright (2004) American Chemical Society).

intermediate priming of the nanocrystal surface with appropriate molecules, such as amino- or thio-silanes, which activate the surface and prepare it for a thick silica coating. Chemical reactions are also possible within the core, *via* diffusion of reactants through the shell layer.[156]

Synthesis of heterodimers and oligomers of NCs

In the case of materials that possess limited miscibility or large interfacial energy, or when only certain regions on the surface of a starting NC are accessible and/or sufficiently reactive, more elaborate NC architectures can form which deviate significantly from the centrosymmetric core–shell type (Fig. 4 and 5). When attempting to grow NCs made of a homogeneous mixture of two materials that are only partially miscible with each other, it is likely that the nanocrystal will grow in a core–shell manner. However, if the interfacial energy between the two materials is large enough, under a sufficient supply of thermal energy a dimer structure can be formed, in which the two materials are phase segregated in two separate particle domains, respectively (Scheme 3, path 1). This concept has been exploited to grow Co–Pd and Cu–In sulfide heterodimers from the co-reaction of the respective molecular precursors under suitable conditions.[157,158] In these cases, the selective nucleation of one material is followed by growth continuation of the second one, which emerges by developing an interface of graded composition.

Another example of minimization of interfacial energy is offered by the nanocrystal heterodimers of γ-Fe_2O_3–CdS and CdS–FePt, which have been synthesized by thermal decomposition of sulfur and cadmium precursors in the presence of preformed γ-Fe_2O_3 and FePt seed nanoparticles, respectively.[59,61] Upon annealing, the highly defective and strained shell of CdS that initially grows on the magnetic nanoparticles coalesces and forms a separate grain, which is attached at one side to the original seed (Scheme 3, path 2). The remarkable point about this type of heterodimer (Fig. 4a) is that it retains both the optical properties of the CdS domain (it shows blue fluorescence) and the magnetic properties of the γ-Fe_2O_3 and FePt domains, and therefore it can be exploited as an interesting bifunctional probe, for instance in biomedical applications.

The ability to tune separately the size of the two single domains in a nanocrystal heterodimer has been demonstrated recently for the Au–$CoPt_3$ system (Fig. 4b and Fig. 5).[159] The dimers were prepared by heterogeneous nucleation of gold on pre-existing $CoPt_3$ NCs (Scheme 3, path 3). The size of the Au and of the $CoPt_3$ domains could be controlled by varying independently several reaction parameters, such as the size of the initial core of $CoPt_3$, the temperature and the molar ratio of gold added per $CoPt_3$ NCs (Fig. 5). It was shown, for instance, that small $CoPt_3$ NCs with sizes of 3–4 nm always promoted the formation of asymmetric dimers carrying large Au domains. On small $CoPt_3$ NCs heterogeneous nucleation of Au was, in fact, difficult and occurred only on a few NCs (Fig. 5a–b). Therefore, the few Au domains that had nucleated could grow to large sizes due to the large availability of Au monomers in solution *via* self-catalyzed Au(III) reduction. On bigger $CoPt_3$ NCs (with average sizes ranging from 5 to 10.5 nm), the nucleation of Au domains was much easier, and therefore a higher percentage of dimers was formed. In these cases, the Au domains in the dimers grew to comparatively smaller sizes, as they had to compete more with each other for the monomers left in solution. The dimers in such cases were more symmetric (Fig. 5c).

Another type of nanocrystal heterodimer is the one based on Au and Fe_3O_4.[160] This was synthesized by thermal decomposition of iron pentacarbonyl in the presence of preformed

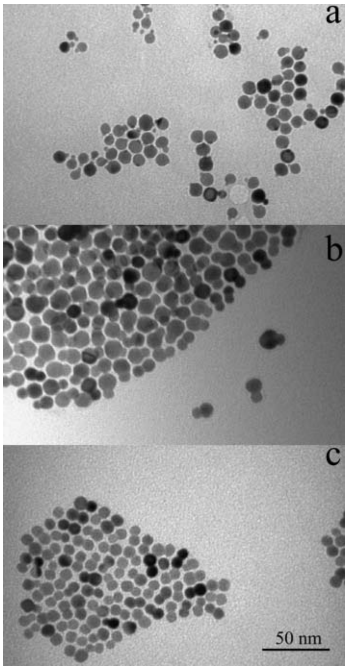
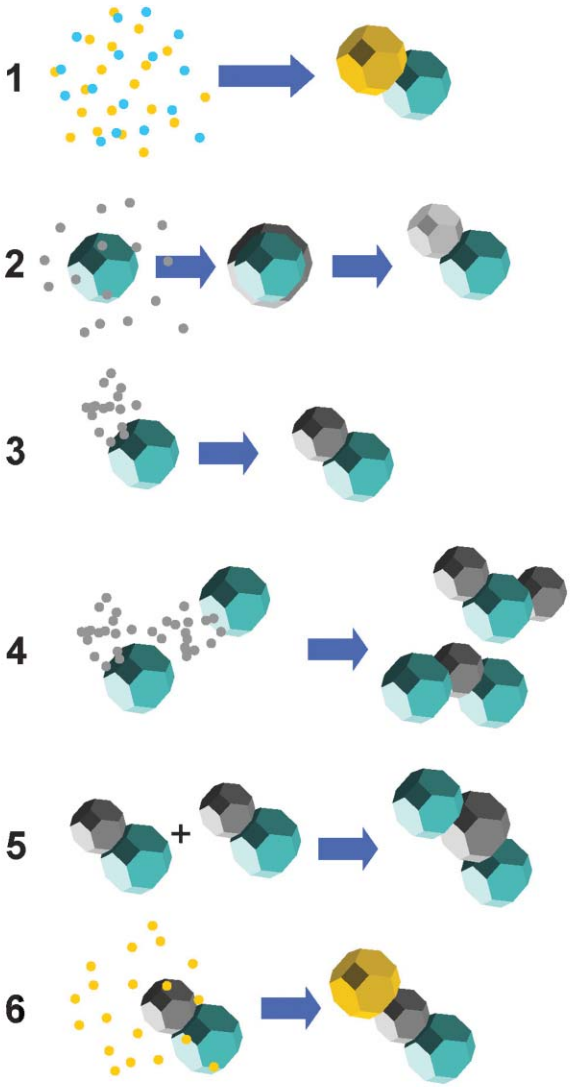


Fig. 5 TEM pictures of heterodimers made of a ferromagnetic alloy domain of $CoPt_3$ and a metallic domain of Au. In (**a**) and (**b**): asymmetric dimers, in which the smaller domain is made up of $CoPt_3$; (**c**) symmetric dimers.



Scheme 3 Sketch of possible mechanisms leading to nanocrystal oligomers: formation of a heterodimer by phase segregation of two immiscible materials (path **1**), by coalescence of an initially amorphous shell (path **2**), or by selective nucleation on a starting seed (path **3**); growth of a trimer upon formation of a domain which bridges two preformed NCs (path **4**); formation of a trimer by fusion of two reactive domains from distinct dimers (path **5**); formation of a trimer by selective nucleation on a preformed heterodimer seed (path **6**).

Au nanoparticles in octadecene, followed by oxidation under air at room temperature (Fig. 4c). Here again the difference in the lattice parameters between Au and Fe_3O_4 explains the formation of the heterodimers (Scheme 3, path 3). In addition, the importance of the solvent effect on the mechanism of dimer formation was demonstrated. In a non-polar solvent, an induced polarization charge at the nanocrystal facet where the iron oxide domain nucleated depleted the remaining gold facets of electrons and thus led to the formation of a dimer-like structure. By performing the reaction in a more polar solvent, the redistribution of the charge over the gold surface led to the nucleation of iron oxide domains on multiple facets, therefore yielding a flower-like structure.

The synthesis of heterodimers based on iron oxide and silver[62] in microemulsions by ultrasonic emulsification represents yet another synthetic route to hybrid NCs. In the reported procedure, in a biphasic system hydrophobic nanoparticles of iron oxide self-assembled at the water–oil interface, providing catalytic sites onto which the Ag^+ ions could be reduced and form Ag nanoparticles. The formation of dimers was explained as dictated by the small surface of the iron oxide NCs that was exposed to the aqueous phase and by the self-catalyzed reduction of the Ag^+ ions only on top of initially deposited silver nuclei (Scheme 3, path 3). Furthermore, this route was extended successfully also to the preparation of Fe_3O_4–Au, FePt–Ag, and Au–Ag heterodimers (Fig. 4d–e).[62] An additional potential of these systems, which was demonstrated in the reported work,[62] was the possibility of selective attachment of different biomolecules on either of the different domains that compose the dimers.

A more systematic investigation of the influence of the lattice mismatch on the formation of hybrid NCs based on γ-Fe_2O_3 and II–VI sulfides has been reported recently.[59] The various types of heterostructures formed were explained in the light of the coincidence site lattice (CSL) theory.[161] The CSL theory is used to identify the preferential orientations of two types of lattice with respect to each other and therefore to explain the crystallographic relationships that are often found at grain boundaries and twins or more in general at the interface between two different crystalline solids. Given two crystal lattices, it is indeed possible that, for specific orientations, some lattice points of one lattice coincide with some lattice points of the other lattice, and a sort of superstructure develops, the so called "coincidence site lattice". Therefore, on the top of a crystal substrate, which exposes a facet with a certain crystallographic orientation, a second material with another type of lattice would tend to grow with its relative orientation being such that at the interfacial plane there should be the best fit in terms of lattice points of the two structures. This match occurs at regular intervals along two directions of the interfacial plane, which will define the two-dimensional cell that describes the interface. The better is the fit between some of lattice points of the two structures and the shorter are the intervals at which it occurs, the lower the interfacial energy will be. In the reported case of the nanocrystal heterostructures based on γ-Fe_2O_3 and II–VI sulfides,[59] the two lattices are the spinel structure for γ-Fe_2O_3 and the sphalerite structure for the II–VI sulfides (both cubic), and the most commonly observed interface was the $(111)_{sphalerite}/(111)_{spinel}$. Along this interface, the coincidence lattice match was particularly good when ZnS was grown on the top of γ-Fe_2O_3 NCs. Indeed, several domains of ZnS could form on different (111) facets of the original γ-Fe_2O_3 NCs (although not with a uniform surface coverage as in core–shell structures), leading to dimers (one γ-Fe_2O_3 particle attached to one ZnS particle), trimers (one γ-Fe_2O_3 particle attached to two ZnS particles), as well as to higher order oligomers, often formed by ZnS domains bridging two or more γ-Fe_2O_3 nanoparticles (Scheme 3, path 4). For CdS growth the match was less favourable, and therefore the majority of the sample was composed of dimers and of isolated particles. Finally, for HgS the match was so poor that only a few dimers were found, while the majority of the sample was composed of isolated particles (the original HgS NCs).

In the case of Ag–Se hybrid NCs,[60] a different approach was followed to control the number of domains of the second materials that are nucleated on a pre-formed nanocrystal. Here, a sequential reduction of the Ag and Se ions caused the formation first of Ag NCs, onto which the reduction of Se ions followed. By varying the concentration of the Se ions, it was possible to synthesize hybrid NCs in which either a single Se nanoparticle or two or more Se nanoparticles were attached to a Ag seed. At high concentrations of Se ions, however, aggregates of several particles were also observed.

An interesting and rather comprehensive approach to hybrid NCs has been reported recently.[162] This work extends several concepts already developed for the synthesis of heterodimers, similar to those described above, to several new combinations of materials and reports many examples of hybrid NCs that can be grouped into four classes: magnetic–metallic, semiconductor–metallic, semiconductor–magnetic, as well as ternary magnetic–metallic–semiconductor. Also the multitudes of geometries that it is possible to attain for the various hybrid NCs (in terms of number of domains, their shapes and their spatial arrangement) are not only a consequence of the interfacial strain, reactivity and miscibility of the materials, but also of the growth conditions, such as solvent polarity, concentration of reactants, and temperature. Two important new approaches are also introduced. In one approach reactions among heterodimers have been triggered, in the same manner as small molecules can be combined to form larger molecules. An example highlighting this concept is the reaction among the so-called peanut-shaped Au–Fe_3O_4 dimers. When heated in the presence of sulfur, the two Au domains from two separate dimers fuse together, yielding a dumbbell-shaped heterostructure, in which a single larger Au domain joins two Fe_3O_4 nanoparticles (Scheme 3, path 5). If the starting Au–Fe_3O_4 nanoparticle is compared to an organic molecule, then the Au domain acts as the reactive functional group that is responsible for the dimerization reaction. Another important concept (which somehow overlaps with the previous one) is that the hybrid NCs themselves can be used as seeds for growing more complex nanostructures. One demonstrated example is the formation of ternary hybrid nanoparticles (Fe_3O_4–Au–PbSe) starting from Fe_3O_4–Au heterodimer seeds (Scheme 3, path 6).

Synthesis of hybrid NCs starting from rod-like seeds

Among the various types of shape-controlled NCs, cadmium chalcogenide NCs are perhaps among the most studied structures, as they can be grown anisotropically in rod-like or in branched shapes with a high control over their geometrical parameters.[6,45] When these materials form in the wurtzite structure in the presence of suitable surfactants, the lateral, non-polar facets can have much lower growth rates than the basal, polar facets, and therefore the NCs can develop preferentially along their unique *c*-axis. Branching can also occur, leading to structures, like tetrapods, in which several rod sections are connected at tetrahedral angles from a branching point. While branching is a common phenomenon in crystal growth, in the present context it is explained both by the occurrence of a cubic sphalerite domain at the central branching region, which is closely related in structure to the wurtzite phase,[45] and by the formation of twins.[163] In both models, the branching is a consequence of the formation of planar defects, either due to a change in the sequence of stacking of atomic layers (the defect is a stacking fault) or to the formation of two or more misaligned domains of the same crystal structures, but which share a low energy interface (a twin plane).

The higher reactivity of the polar facets (the tips of rods or of tetrapods) of such anisotropic NCs opens up the possibility of nucleating a second material exclusively at these locations (Fig. 6). One additional peculiarity of the wurtzite structure is the absence of a plane of symmetry perpendicular to the *c* axis, and therefore the two basal sides of a given rod are not chemically equivalent. One can therefore expect significant differences in reactivity between the two tips. This diversity has been recently highlighted in the lateral growth of sections of a second semiconductor material on a starting semiconductor nanorod.[68] By playing with the reaction conditions, it has been demonstrated that it is possible to decide whether such additional growth will be linear (so the second material will grow in a rod shape) or whether a branching point will be introduced at the interface between the two materials. For instance, one can start either from a rod or from a tetrapod, and then grow a second material on it, either in linear or in branched fashion. In Scheme 4 some of these possibilities are reported. Starting from one rod, either both ends of the rod are continued in a linear manner (Scheme 4, path 1), or one end is continued in linear manner and at the opposite end a branching point tends to be generated, from which three distinct arms are formed (Scheme 4, path 2). Both possibilities have been demonstrated in the case of hybrid CdS–CdSe, CdS–CdTe and CdSe–CdTe NCs.[65]

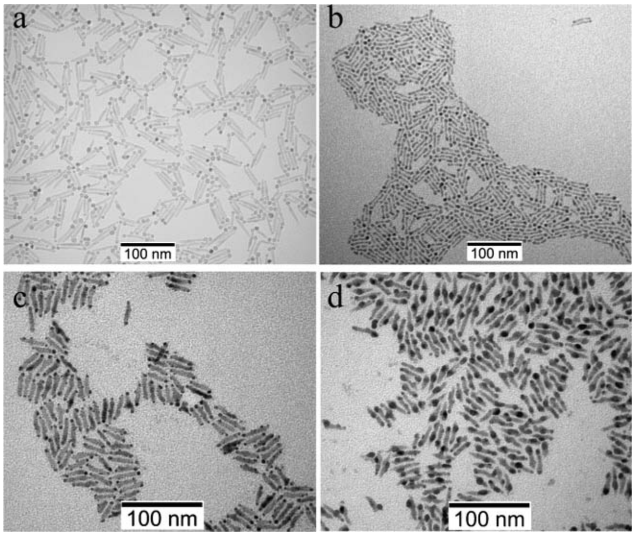
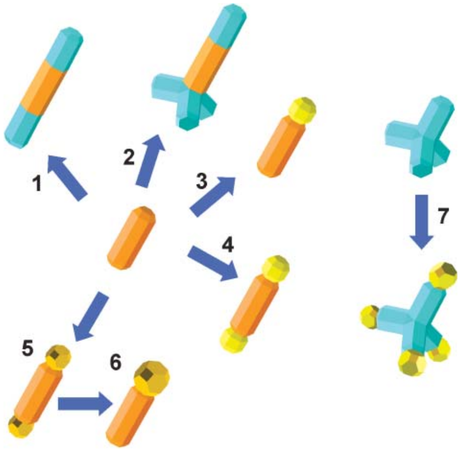


Fig. 6 TEM images of nanocrystal heterostructures based on rod-like seeds: (**a**) CdSe nanorods with PbSe tips located at both ends; (**b**) CdS nanorods with one PbSe tip; (**c–d**) CdSe nanorods with two or one Au domain, respectively.

The difference in reactivity among the various facets of wurtzite nanorods has been clearly demonstrated for CdS nanorods, as a PbSe domain could be grown either on both tips or just on one tip of a rod (Fig. 6a–b), by carefully adjusting the synthesis conditions (Scheme 4, paths 3 and 4).[57] PbSe domains, which formed in their typical rock-salt structure, showed a preferential orientation with respect to the substrate. In the majority of heterostructures based on CdS or on CdSe, the 002 planes of PbSe rock salt were aligned with the 100 planes of CdS or CdSe wurtzite.[57] The reasons underlying the large differences in reactivity among the various facets of the wurtzite structure, which allow for the selective growth on the tips of the rods, are still under investigation. So far, the indication is that this is driven by the difference in the binding energy of the surfactant molecules to the different facets.



Scheme 4 Sketch of possible paths leading to complex nanocrystal heterostructures starting from rod-like seeds: a rod-like seed can be continued either in a linear manner at both ends (path **1**), or in a linear manner at just one side and with a branching point at the opposite side (path **2**), or with one (path **3**) or two spherical terminal tips (path **4**); a dumbbell-like heterostructure (path **5**) can evolve into a matchstick-like structure *via* an intra-particle Ostwald ripening (path **6**); a tetrapod-shaped nanocrystal can be functionalized with a spherical nanocrystal at each of the four terminations (path **7**).

Recently, nanocrystal heterostructures that resemble a dumbbell have been synthesized by the solution growth of gold tips (Fig. 6c) at both ends of a semiconductor nanorod (Scheme 4, path 5).[4] Following this work, it has been observed that the nano-dumbbell represents an intermediate structure, which can evolve into a heterostructure (Fig. 6d) that has only one end covered by a gold tip (Scheme 4, path 6). This behavior resembles an effect known in colloidal science as "Ostwald ripening", in which bigger particles tend to consume the smaller ones.[79] Unusually, the ripening here appears to occur only between the two gold tips of a single nano-dumbbell. The driving forces for this effect arise from the surface energy and the size dependence of the redox potential. The smaller gold tip is more unstable as it has both higher surface energy and stronger susceptibility to oxidation compared to the larger tip. For growth or ripening to occur, gold atoms attached to one tip have to go back into the solution, and this only becomes possible if they are oxidized to metal ions. When this happens, electrons are released to the gold tip and they shuttle all the way across the dumbbell by hopping through surface states. Once they reach the bigger tip, they are used to reduce gold ions present in the solution, which deposit on that tip and make it grow. The process stops when the smaller gold tip disappears completely. At this point no ripening among different hybrid NCs can occur, as electrons cannot travel through the solution. As the model developed by the authors shows, fluctuations in the initial growth of dumbbells cause a large fraction of them to have gold tips of dissimilar sizes. Interestingly, this evolution is not observed when electrons cannot travel through the nanocrystal, as in the case of a nano-tetrapod. The central section of the tetrapod contains several defects that act as a barrier for the free movement of electrons. Therefore, only simultaneous growth of four gold tips occurs in tetrapods, with no ripening (Scheme 4, path 7).

Selective functionalization of only one arm of a CdTe tetrapod was achieved recently by depositing tetrapods on a substrate and by partially covering them with a polymer layer, so that the fourth arm (the only one not touching the substrate but pointing upwards) protruded out of the polymer layer.[164] This arm could be selectively functionalized with Au NCs. Although the Au domains are bound to the CdTe NCs through organic linkers, a similar strategy could be followed to nucleate directly a Au domain on the exposed arm tip *via* reduction of a Au(III) salt, in analogy with the case of CdSe nanorods.

Finally, an extended strategy to access several types of Au-tipped dumbbell-like nanocrystal heterostructures has been developed recently, which involves the selective oxidation of either PbSe or CdTe sacrificial domains, initially grown on CdSe and CdS nanorods, with a Au(III)–surfactant complex.[165] This approach allows one to grow Au domains onto specific locations of anisotropically shaped NCs for which direct metal deposition is unfeasible, as for the case of CdS nanorods. This strategy could be especially appealing to create other types of complex colloidal nanoheterostructures, provided that a suitable sacrificial material is grown on top of the starting nanocrystal seeds.

Perspectives of hybrid NCs

Nanocrystal heterostructures in which spherical, rods or branched sections of different materials are connected in a deliberate geometry, without the need of weak organic molecules as linkers, can uncover new and exciting applications, ranging from nano-electronic to optoelectronic, biomedical, photovoltaic and catalytic applications. By carefully selecting the materials composing the heterostructure, one could design, for instance, a system in which two or more quantum dots are coupled through a barrier of tuneable height and width, as has been demonstrated for the case of two CdSe or PbSe domains grown at the ends of a CdS rod.[57,65] Alternative arrangements of materials can lead to structures that perform the tasks that are typical of a transistor, with the difference that these structures come already self-assembled from the solution and in huge numbers.[65] The possibility to grow gold NCs at the terminations of rods and tetrapods has paved the way in this direction.[56,58] Gold tips can be used, for instance, to connect more easily these structures to macroscopic electrodes, or to facilitate their self-assembly in solution. If coupled through their Au domains with biological molecules capable of molecular recognition, these Au-tipped NCs could be chained together.[56] In principle, such a strategy could lead to the creation of much more complex assemblies. A similar type of approach was proposed some years ago for assembling segmented nanowires,[125] as in that case a selective surface functionalization of the nanowires was based on the different affinities of the various wire sections towards different molecules/biomolecules. Ultimately, it would be possible to realize nanocrystal assemblies that would behave as nanomachines, equipped for instance with magnets for navigation or magnetic detection, fluorescent regions that could enable them to be tracked optically, as well as bearing molecular receptors and chemical releasing agents for biological recognition and targeting. Up to now, only a few examples of such biological applications of hybrid nanostructures prepared by synthetic routes have been demonstrated,[62,71] although we envision a wide range of applications which can exploit hybrid nanostructures for solving biological problems.

So far, the types of hybrid nanocrystal architectures that can be realized are quite primitive and not fully controlled. In these types of NCs, the interface between two domains is expected to be very defective and clear epitaxial relationships do not always exist, with possible detrimental effects on the overall properties of the system. In addition, in some cases the growth of one material on the top of a crystalline core can kill the properties of the original nanocrystal, such as for instance, the fluorescence efficiency of CdSe nanorods when Au domains are grown at their tips.[56] Therefore, insulating domains would need to be built in between, if fluorescence efficiency needs to be conserved, further complicating the synthetic procedure. It is clear that this field is still in its infancy, and that significant progress must be made in materials science for a new generation of NCs to be truly exploitable in viable applications.

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