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FEATURE ARTICLE

Chemically induced self-assembly of spherical and anisotropic inorganic nanocrystals

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The self-assembly of inorganic nanoparticles is a research area of great interest aiming at the fabrication of unique mesostructured materials with intrinsic properties. Although many assembly strategies have been reported over the years, chemically induced self-assembly remains one of the dominant approaches to achieve a high level of nanoparticle organization. In this feature article we will review the latest developments in assembly driven by the active manipulation of nanoparticle surfaces.

Introduction

The mechanical strength of spider silk,[1] the peculiar optical properties of photonic structures[2] or the synergetic effects of bacteria assemblies[3] are only few examples where the self-assembly of individual objects results in new functional materials. The organization of objects at the mesoscopic scale is a current paradigm of materials science because it allows the synthesis of structures with novel properties derived from the cooperative interactions of the individual components. Among the different types of assembly components, the use of inorganic colloidal nanocrystals (NCs) is of particular interest because of the various synthetic routes available to manipulate their size, shape and composition, offering the ability to tune their physical and chemical properties.

For scientists to build new materials from bottom-up or mimic natural self-assembly, the balance of forces defining the desired structure should be designed on demand. This led to the idea of directed assembly.[4,5] The directed assembly is defined as a "process whereby an intrinsically self-assembling system is aided or modulated using directing agents, external fields or templates."[5] To date many different approaches have been used to control and direct self-assembly of NCs. Notable strategies include those based on prefabricated templates,[6] small-molecule[7,8] and electrostatic interactions,[9] solution-deposition methods,[10] nanowelding,[11] and bio molecular tools.[12–14] Each of

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these methods offers alternative pathways towards self-assembly and leads to a variety of structures with different sizes, shapes, and architectures.[15,16] Potential applications of such arrays range from scaffolds for biological systems to the elements of data storage devices, photodetectors, light-emitting diodes and solar cells.[17]

In this article we chose to highlight recent developments on methods to direct the self-assembly through manipulation of NCs surface by means of chemical stimuli. Such approaches offer the opportunity to achieve a high level of control on the fabrication of larger structures. It is hard to define specifically when such strategies have been realized in practice for the first time. One of the proof-of-concept examples dates back to the rational assembly of gold nanocrystals into macroscopic materials using DNA.[18,19] Since then the field of chemically induced self-assembly (CISA) of NCs has grown steadily. This fast progress brought exciting discoveries as well as new ideas of how to further develop the available tools for the CISA. For the purpose of this article we find it reasonable to divide CISA into two classes, namely, assembly through chemical linking (*i.e. via* small molecules, DNA, peptides) and ligand destabilization (*i.e. via* ligand replacement).

DNA-mediated organization of gold nanoparticles is a typical example of CISA *via* linking. It combines specific chemical interactions (*e.g.* gold–sulfur bond), precise recognition of complementary DNA strands *via* hydrogen bonding and offers a versatile template for further manipulation.[12] For example, it has been shown that monodisperse Au NCs functionalized with DNA strands could be assembled and disassembled by action of enzymes in a highly ordered fashion.[13,14] This approach allowed not only the design of reversible assembly of one type of NCs, but also the induction of high selectivity towards the size of NCs and interparticle distance. Kiehl, Seeman and co-workers[20–22] used pre-fabricated two-dimensional DNA scaffolds to drive the assembly of gold NCs into arrays with controlled interparticle separations (*i.e.* long in one direction and short in another) as well as arrays tiled with 5 nm and 10 nm diameter Au NCs. Recently, using a triangular DNA origami template Ding *et al.*[23] were able to assemble six different sized Au NCs into linear structures where NCs positions and separations were predefined by the initial design of the experimental system. Furthermore, the authors tested a theoretical prediction regarding field enhancement effects in the linear chains of metallic spheres with different sizes.

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Creating specific reaction sites on the surface of NCs *via* ligand destabilization is another attractive direction. This approach turns ligand capped NCs into active species, which can be connected in a defined fashion *via* chemical interactions, similar to polymerization of organic monomers. Recently, Liu *et al.*[24] showed that gold nanorods asymmetrically functionalized with polystyrene units self-organize into chains if the quality of solvent altered an analogue process to step-growth polymerization.

The above examples illustrate new opportunities in the design of innovative functional inorganic nanostructures *via* CISA and re-emphasize the importance of rational alteration of the NCs surface. In the following parts of this feature article we discuss the concepts that govern the nanocrystal surface chemistry and then overview recent experimental examples where these concepts are applied to selectively manipulate ligands and drive the self-assembly of various nanoparticles.

Role of surface and ligands in nanocrystals self-assembly

Surface of nanocrystals

The surface of colloidal NCs is a boundary that separates the solid phase (NCs core) from the environment (*i.e.* bulk of solution) and is formed by the outermost atomic layer of the nanocrystal core. The surface atoms of nanocrystals exhibit high chemical reactivity due to the number of dangling bonds in comparison to the surface atoms in the bulk.[25] Thus it is reasonable to expect for the surface of nanocrystals to play a significant role in the self-assembly. The actual structure as well as the chemical composition of nanocrystal surface atoms defines the way the particle interacts with specific types of ligands. Therefore, the ability to control the positioning and type of the surface atoms offers the possibility to tune the interactions of molecules with the nanoparticle surface. For example, the stoichiometry of binary NCs (alloys, oxides *etc.*) depends on the synthetic conditions and results in surface atoms with different coordination properties. Jasieniak and Mulvaney demonstrated how the stoichiometry of the CdSe NCs surface could be controlled from Cd- to Se-rich by combining a phosphine-free selenium precursor with the successive ion layer adhesion and reaction method (SILAR) using the classical hot injection approach.[26] The derived NCs exhibited selective affinity towards different capping molecules. Amine-coated Cd-rich NCs were subjected to the addition of trioctylphosphine selenide and hexanethiol but did not interact with trioctylphosphine, while Se-rich NCs behaved in the opposite way (Fig. 1A and B). An understanding of such synergism between surface and ligands has important consequences for the properties of assembled materials. For example, citrate species bound to the surfaces of apatite nanocrystals can regulate the biomineralization process,

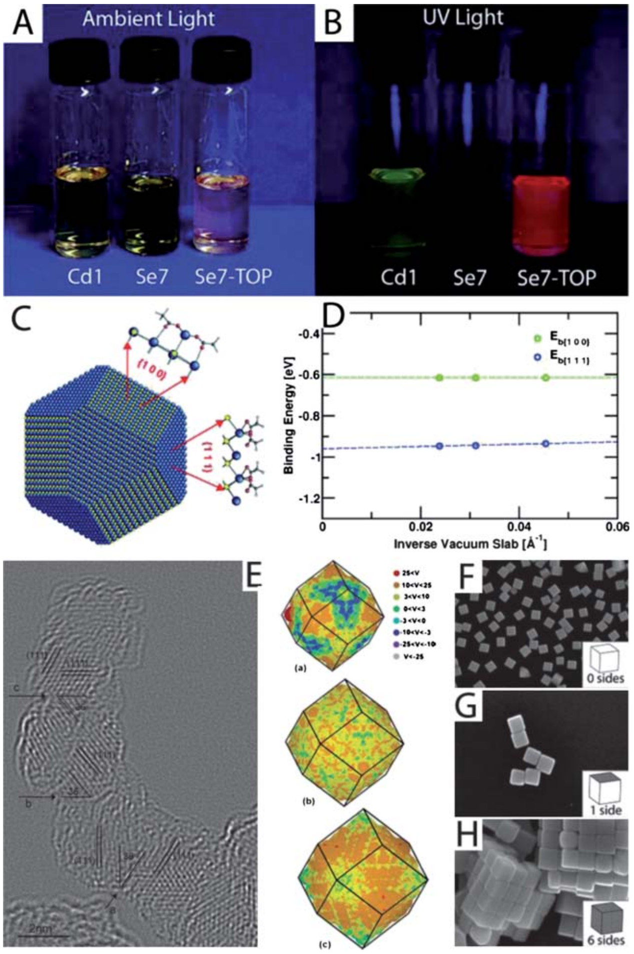

Fig. 1 Surface effects in NCs properties and assembly: solutions of CdSe NCs with Cd- and Se-rich surfaces (Cd1 and Se7 respectively) under ambient (A) and UV (B) light, notice that addition of TOP to the Se-rich NCs induces visible boost (200-fold) in the luminescence quantum yield (sample Se7-TOP);[26] (C) scheme of the binding of lead acetate ligand to the chemically non-equivalent facets of PbSe NC and (D) calculated binding energies which show that ligand binds stronger to [111] facet;[29] (E) HRTEM image of chain-like assembly of nanodiamonds formed by electrostatic attraction between specific facets and simulation of the size-dependent surface electrostatic potential respectively;[30] (F–H) SEM images of silver nanocubes (approx. 97 nm edge length) self-organized into different configurations depending on the number of hydrophobically functionalized facets (rendered dark in the corresponding insets).[31] Reproduced with permission from ref. 26 and 29 (ACS), 30 (RSC) and 31 (Wiley).

which defines the interfacial compatibility of an inorganic material with a protein and altogether is critical in setting the optimal mechanical performance of resulting biomineral nanocomposite (*i.e.* apatite in bone).[27,28]

The role of the nanocrystal surface is especially important if anisotropic or faceted NCs are considered. The reason is that different crystal facets can exhibit different configurations of surface atoms, increasing the possibility of alterations in parameters important to self-assembly (*i.e.* chemisorption[29] (Fig. 1C and D) and nanocrystal electrostatic properties[30] (Fig. 1E)). For example, Xia and co-workers were able to control the organization of Ag nanocubes (mean edge length of 97 nm) into five different assembly geometries by preferential modification of their side facets with hydrophobic/hydrophilic ligands (Fig. 1F–H).[31]

Other surface effects[4,32] such as adsorption of atoms or molecules to the surface of NCs, surface melting, and high surface energy due to several dangling bonds[33] can find potential use as tools for bottom-up fabrication of nanostructured solids *via* coalescence in solution (*i.e.* "molecular welding"[34]) or solid state sintering.[35,36]

Capping ligands

The properties of ligands that interact with the nanocrystal surface are equally important to the physical characteristics of the NCs and play a pivotal role in the nanoparticle self-organization. The ligands can be chemisorbed on the nanocrystal surface creating chemical bonds or physisorbed *via* electrostatic or van der Waals interactions. Usually, ligands are introduced during the synthesis of NCs as agents to control the nucleation and growth rate. Moreover, they provide colloidal stability for the final product and affect the physical and chemical properties of the NCs through selective absorption and passivation of surface dangling bonds.[37–39] For example, the size and chemical composition of the capping molecules can influence the dipole moments of the particles, their solubility and reactivity, directing their self-assembly *via* electrostatic interactions[40,41] or specific covalent bonding (Fig. 2A and B).[42,43] Typical examples of surfactants include alkylphosphonic acids, fatty acids and amines, thiols, and phosphines.[44]

The importance of the capping ligands should not be neglected or underestimated.[45–48] Very often it is thought that the surface capping layer of as-synthesized NCs is made of the major surfactant component in the reaction mixture. However, advanced studies focused on the determination and understanding of the composition of capping layers around colloidal NCs uncovered a more complex surface structure. For example, in a recent comprehensive study Cros-Gagneux *et al.* showed that InP quantum dots synthesized from relatively simple precursors had an unexpected organic structure consisting of two co-ordination spheres. The first coordination sphere was composed of tightly bound palmitate ligands, which displayed two different bonding modes. A second coordination sphere included a dialkyl ketone and residual long-chain non-coordinating solvents (ODE and its isomers), which interacted through weak intermolecular bonds with the alkyl chains of the carboxylate ligands (Fig. 2C and D).[49]

Another critical parameter for nanoparticles organization is the actual concentration of capping ligands. Several reports show that a large excess of free ligands can drive the nanocrystal assembly and improve the quality of NCs superlattices (Fig. 2E and F).[50–55] An assumption is that the remaining free ligands provide an extra driving force (*e.g.* depletion[56]), which organizes the crystals to thermodynamically stable structures. In a similar manner, in aqueous solution, an excess of ligand molecules affects the electrostatic interactions between charged particles forcing them to organize into various network-like structures, as was extensively demonstrated for Au NCs.[57–59]

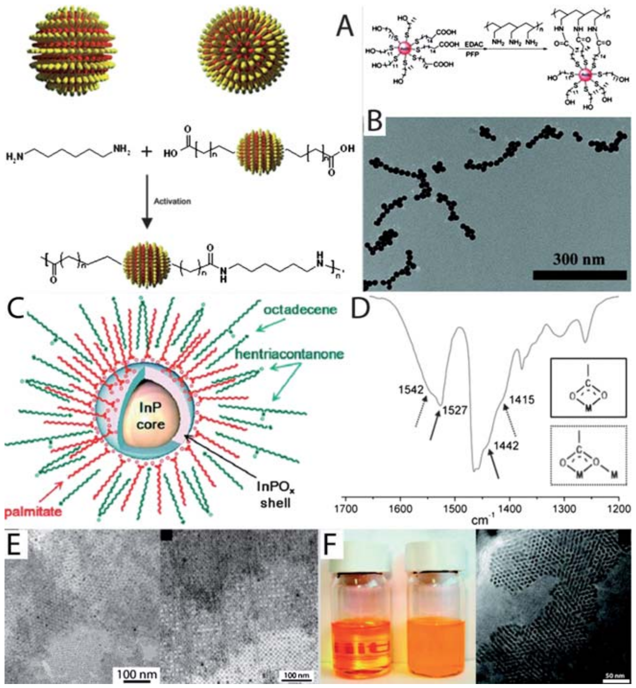

Fig. 2 Ligand contribution into assembly and structure of NCs. Formation of linear chains from rippled asymmetrically functionalized Au NCs through formation of amide bond[43] (A, scheme) or by covalent linking between capping molecules and polymer template[42] (B, with corresponding TEM inset); schematic representation of complex multilayered structure of InP NCs (C) and corresponding FTIR spectrum (D) detecting the presence of two-binding modes for palmitate ligand;[49] TEM images of dried mixture of Au and Fe_2O_3 NCs phase-separated (E, left inset) or self-organized into AB_2 superlattice (E, right inset) if excess of oleic acid introduced in the latter case;[51] (F) colloidal CdSe/CdS core–shell nanorods readily assemble in solution upon addition of free oleic acid, as can be observed visually (F, left inset) and confirmed by Cryo-TEM investigation[56] (F, right inset). Reproduced with permission from ref. 43 (AAAS), 42, 49, 51, 56 (ACS).

Overall, the success of the bottom-up assembly requires a basic knowledge of the surface chemistry of nanocrystals as well as a good understanding of the surfactants' kinetic and thermodynamic characteristics. Having described the basic properties of nanocrystal surface chemistry and capping ligands, in the following paragraphs we will elaborate our discussion on specific examples of CISA of colloidal nanocrystals.

Assemblies of spherical nanocrystals

Due to the ease of preparation, colloidal NCs of spherical shape are regularly employed as building blocks in self-assembly. Close-packed, mono- and multilayered superlattices of spherical colloidal nanocrystals are extensively discussed in literature and we direct the reader to the following reviews[10,60,61] and references cited therein for more information. On the other hand, to drive the organization of spherical NCs into one, two, or three-dimensional structures such as chains, loops or branched networks is a more complex task and usually requires chemically directed approaches.[62]

One of the ways to chemically induce the anisotropic self-organization of nanocrystals is by the manipulation of covalent, non-covalent or electrostatic interactions between the surface ligands of adjacent particles. Such interactions can be facilitated either by small molecules, which *via* reversible or irreversible forces can organize particles or by destabilization of the nanoparticle capping ligand shell. Ligand destabilization leads to a substantial increase in the attraction potential between nanoparticles and results in their assembly. By using these strategies it is possible to convert originally isotropic and inert NCs into 'reactive species', which can organize themselves into oligomers (dimers, trimers, tetramers, both planar and 3D), long and short chains, as well as branched structures, as will be discussed below.

Many research groups employed biomolecules as a tool to organize particles into a variety of anisotropic mesostructures with high degree of control over the assembly process.[63] For example, in recent studies DNA was used to direct the organization of colloidal quantum dots (QDs) and metallic particles (mostly Au) in discrete assemblies (Fig. 3A).[64] Liu and co-workers were able to further manipulate these structures by varying the Au/QD ratio within an individual nanostructure, and by tuning the particle size or the separation distances between the particles.[65] The authors found that all these factors affect the photonic interactions between gold and QDs and suggested the possibility to employ these materials in photonic applications. In another study, Mastroianni *et al.*[66] demonstrated a remarkable

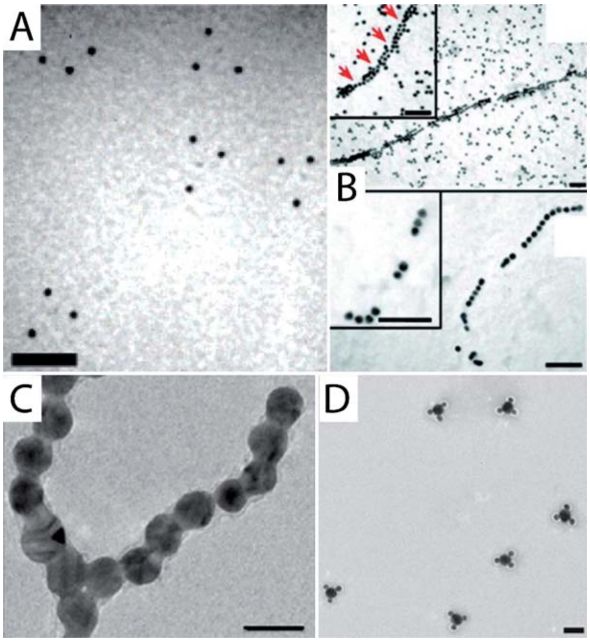

Fig. 3 Representative gallery of TEM images of chemically induced assemblies of spherical NCs: (A) discrete assemblies of CdSe@ZnS-$(Au)_3$ induced by DNA hybridization (scale bar 100 nm);[64] (B) arrays of peptide-functionalized Au NCs assembled along a DNA template[67]—the red arrows indicate possible helical twists in nanoparticle arrangements (scale bar 100 nm); (C) fragment of Au NCs chain formed *via* ligand destabilization and encapsulated within thin silica shell[84] (scale bar 20 nm); (D) AB_3 binary nanoclusters of Au NCs formed by tuning of the charge repulsion[86] (scale bar 50 nm). Reproduced with permission from ref. 64 (ACS), 67, 84 (RSC) and 86 (NPG).

degree of control over the organization of gold nanoparticles of different sizes into three-dimensional pyramids using DNA. Due to the versatility of DNA species, the authors suggested the use of these nanostructures as three-dimensional plasmonic rulers. On the other hand, Kanaras and co-workers[67] used the interactions between specific peptides and oligonucleotides to organize gold nanoparticles into anisotropic structures (Fig. 3B). Gold nanoparticles coated with DNA-binding peptides were attached to self-organized oligonucleotide templates to formulate well-ordered structures of nanoparticles. By regulating the amount of DNA-binding peptide attached to the nanoparticle surface, the nanoparticle assembly was controlled to form dimers, trimers, and adjustable-length nanoparticle chains as well as more complex structures.

All the above ways that were used to organize nanocrystals can be employed to realize even more elaborated three dimensional structures with the goal to create smart nanodevices.[68] Research groups showed that DNA- or protein-directed assembly can provide the means of arranging particles into complex structures, such as 3D tubes[69] and non-compact mono- and binary superlattices.[70–73] Recently, Gang and co-workers managed to introduce an additional level of control in self-assembly using DNA and a molecular stimulus (single DNA strand) to modulate the interparticle distances in superlattices, while preserving structural integrity.

It is clear that the use of biomolecules to organize nanoparticles offers the ability to control several characteristics of the derived smaller or larger assemblies that is not possible to manage with other approaches. However, sometimes the inherent complexity of biomolecules requires elegant manipulation of the active species, which is not always favourable for applications.

An alternative approach to biomolecule-driven assembly is based on the non-covalent interactions between small organic molecules. Recently Stoddart and co-workers employed a TTF-DEG/CBPQT^{4+} [(diethyleneglycol disubstituted tetrathiafulvalene/cyclobis (Paraquat-*p*-phenylene)] host–guest binding motif to guide the assembly of small Au NCs into homodimers, trimers and tetramers.[74] These oligomers could be either assembled/disassembled electrochemically, using the two electron reduction/oxidation of TTF or irreversibly fused into a one solid Au nanoparticle by thermal treatment (using HR-TEM).

Halogen bonding (XB) is another chemical strategy to assemble materials *via* non-covalent interactions. This method was first used in supramolecular chemistry for the organization of small molecules[75] and it was recently applied to the NCs self-assembly. XB is an interaction occurring between a halogen atom (electrophile agent) and a Lewis base. To utilize it in the NCs assembly process, Shirman *et al.*[76] functionalized Au NCs with a fluorinated aromatic compound (halogen donor) and triggered their assembly by adding bifunctional linkers of pyridine moieties. The same group reported the controlled assembly of citrate-capped Au NCs using cross-linkers containing a different number of pyridyl groups, stressing that assembly was mainly due to the coordination of pyridyl groups to the electrophylic surface of metal particles rather than due to weak intermolecular interactions.[77]

Non-covalent forces are generally weak but vary in the strength.[78] For example, Coulomb interactions are in the range of 250 kJ mol^{-1}, while hydrogen bonding, π–π stacking, and dipole–dipole forces are in the range of 0–65 kJ mol^{-1}. Thus, assemblies created using these types of forces might not be stable under stringent conditions or at high temperatures. On the other hand, covalent bonds are generally stronger (up to 400 kJ mol^{-1}), and irreversible. Therefore, they are usually employed to create stronger and more stable assemblies.

Several covalent linking strategies were proposed to direct NCs assembly. For example, azo- or amido-couplings were employed by Maneeprakorn *et al.*[79] for making dimers, trimers and tetramers of different-sized Au NCs as well as their hybrids with Ag, CdS and CdSe. In another study, Au NCs were functionalized with 4-aminothiolphenoxide and conjugated to fullerenes. The C_{60}–Au NCs assemblies could be used to fabricate films that were very sensitive to UV illumination.[80] Such assemblies can be of great importance for applications in consumer electronics, where the products are required to last long in harsh conditions. Recently, Chaikin *et al.*[81] reported that metal ions could also be used as efficient linkers. The authors prepared multilayered films from hydroxamate-functionalized Au NCs and Zr(VI) ions. Zirconium cations served as coordination bridges. The main advantage of this inorganic complex-driven assembly was that the interparticle distance in the films could be tuned *via* layer-by-layer deposition with a precision limited by the length of the hydroxamate/Zr(IV) coordination unit (~1.3 nm).

The assembly of nanoparticles *via* ligand destabilization is mainly based on electrostatic forces. The assembly is triggered when the capping layer of ligands is not sufficient to prevent nanoparticles from agglomeration. This can happen when the number of surface ligands is smaller than what is needed to keep the colloids stable or when they are partially displaced by another ligand. Hence, destabilization of the capping ligand layer can be employed to deliberately control the kinetics of NCs organization and drive the assembly into the fabrication of anisotropic structures (*i.e.* clusters, chains, and networks).

Several strategies to guide self-assembly *via* ligand destabilization have been developed, both in water and in organic solvents. For example, Mann and co-workers produced robust nanoparticle chains upon addition of 2-mercaptoethanol (MEA) to citrate capped gold nanoparticles.[82,83] The assembly was driven by dipole–dipole nanoparticle interactions. The authors studied the kinetics of the nanoparticles' formation and attributed the presence of the dipoles to the partial MEA/citrate capping of Au NCs (possibly due to the unequal spatial distribution of Au–S bonds, reminiscent of Janus particles).[83] The dipole–dipole driven nanoparticle assembly was recently universalised to include the *in situ* polymerization of the surface attached ligands, which produced enveloped nanoparticle networks (Fig. 3C) with retained nanoplasmonic properties and enhanced stability in temperature and pH-variations.[84]

An alternative approach for making anisotropic structures of spherical NCs through ligand destabilization is based on the tuning of the electrostatic repulsion between likely charged NCs in solution. Cho *et al.*[57] described a method to control the length and interparticle separations of chainlike gold nanoparticle assemblies. The chainlike structures were driven by adding HS $(CH_2)_nCOOH$ (n = 2, 10, and 15) to a solution of Au NCs in a mixture of ethanol and water (98:2 by volume). The number of

Au NCs in the chains could be manipulated by varying the concentration of the thiol. On the other hand, the interparticle distance between the particles could be adjusted by using thiols of different chain lengths. The anisotropic growth of Au NCs chains (without an apparent force directing organization of particles) was explained by the lower electrostatic potential at the end of the NCs oligomers *versus* higher potential at its side. The latter explanation was adopted from the work by Zhang and Wang[85] who showed that the electrostatic repulsion between Au NCs could be controlled by alteration of the ionic strength and especially the polarity of the colloidal particles. As an example, the authors illustrated the regulation of the length of nanoparticle chains. These chains derived from destabilization of thioglycolic acid-capped Au NCs upon addition of NaCl. Wang *et al.*[86] were able to tune the charge repulsion between nanoparticles of different sizes in order to form nanoparticle oligomers with controllable stoichiometries (Fig. 3D). Specifically, it was found that higher ionic strength lowers the electrostatic repulsion between NCs thus leading to AB_n oligomers of higher n number.

In organic solvents NCs are usually stabilized by the steric repulsion between bulky capping molecules. In this case, the controlled removal of these ligands from the NCs surface is the driving force for the nanoparticle self-organization. Recently Larsen *et al.*[87] were able to controllably produce well-defined aggregates of superparamagnetic iron oxide nanoparticles (SPION) by partial destabilization of the native capping shell of heptanoic acid with acetic acid. According to the proposed mechanism of aggregation, the interaction between the surface of SPION and acetic acid is strong and leads to the partial substitution of the heptanoate moiety. The shorter acetate significantly reduces the steric hindrance between particles thus resulting in their controlled aggregation. In another work, Stolarczyk *et al.*[88] exposed a stable solution of oleic acid-capped SPION to a cyanopropyl-modified silica layer and observed the gradual removal of the NCs surfactant, which was adsorbed by the silica. The 15 nm SPION were progressively destabilized and aggregated in clusters with an average hydrodynamic diameter ranging from 60 to 200 nm. The authors explained that the reason for the nanoparticle clustering is the gradually reduced steric repulsion, which derives from the competitive stabilizer desorption by the silica phase. Based on this strategy, the same group recently demonstrated an assembly of binary NCs clusters composed of Au or $CoFe_2O_4$ NCs and SPION particles.[89]

In this section we have discussed several strategies to form nanoparticle assemblies that are driven by the manipulation of ligands bound to the surface of spherical nanoparticles. These strategies are important because they introduce new ways to master the programmed organization of nanoparticles with the hope that some of these ways will be useful for fabricating devices operating in the sub-wavelength region. One of the advantages of some assemblies presented here is that certain physical properties of the NCs (*i.e.* optical) show the most pronounced cooperative effects when particles are coupled together. The most notable example of such effects is the plasmon coupling between metal NCs. For example, an additional longitudinal plasmon band appears at 700 nm when individual spherical Au NCs (11 nm in diameter, $\lambda_{abs} = 520$ nm) assemble into 1D chains. This transformation is accompanied by the change in the colour of colloid solution from pale red to purple-blue.[90]

The measurable characteristics of the plasmon coupling (*i.e.* the position and intensity) are sensitive to the chemical composition of the interacting particles (*i.e.* Au–Au or Au–Ag), the number of particles participating in the assembly, their arrangement in space and the medium in which they are dispersed. Regulation of these characteristics can result in a range of applications from sensors and molecular rulers[91,92] to sophisticated plasmonic waveguides and optical antennas.[93] This emerging field is also known as "self assembled nanoplasmonics".[94]

Assemblies of anisotropic nanocrystals

The anisotropic NCs have very interesting properties, which make them potential candidates for several applications. The synthesis of NCs with precise control of their shape is a dynamically developing branch of nanochemistry.[95–97] Among the variety of shapes, rod-like NCs of noble metals, semiconductors and magnetic materials are the most studied anisotropic particles, in terms of their physical properties. For example, the electronic structure of seeded growth II–VI semiconductor nanorods[98] and the optical properties of anisotropic gold NCs[99] are well-described and quite understood. For more details and up to date discussion of the physical properties and applications of elongated inorganic NCs we refer the reader to a recent comprehensive review on this topic.[100]

For the formation of close-packed superlattices and liquid crystalline-like assemblies of anisotropic NCs, we recommend several book chapters and reviews discussing this area in greater detail.[101–104] As in the case of the previous section for spheres, the chemically driven assembly of anisotropic particles emerged in the past few years as a powerful new approach to fabricate elegant particle arrangements such as oligomers, ribbons, circles and chains.[105] In this section we review several examples of chemically driven nanoparticle assemblies, where the nanocrystals have various shapes, *i.e.* tetrapods and multi-branched structures, rods, sheets and other morphologies.

For this type of NCs the combination of shape anisotropy and chemically induced linking can offer an additional level of control in self-assembly, driven by structural selectivity and chemical tuneability. The Mirkin group recently demonstrated this concept for gold nanorods, prisms and polyhedrons. Among other findings, the authors reported a remarkable level of control in positioning Au nanoprisms to form assembled 1D mesostructures (Fig. 4A and B). The accuracy in face-to-face distance between the triangular prisms could be easily controlled by the length of the chemical linking (DNA hybridization).[106] The authors highlighted the fact that it would be very difficult to achieve such precision using top-down fabrication techniques. In another study, Kim and Lee demonstrated the assembly of DNA–Ag nanoprism conjugates into two different arrangements (edge-to-edge/face and face-to-face) and their further utility in colorimetric sensing of oligonucleotides.[107]

In contrast to the relatively 'soft' biomolecular bonding, the CISA can also be realized by forming solid inorganic junctions between anisotropic NCs. This strategy has been demonstrated by Figuerola *et al.* for gold-tipped semiconductor nanorods, bullets and tetrapods.[11] At first, anisotropic NCs of choice (CdSe, CdSe@CdS, ZnSe@CdTe) were decorated with small

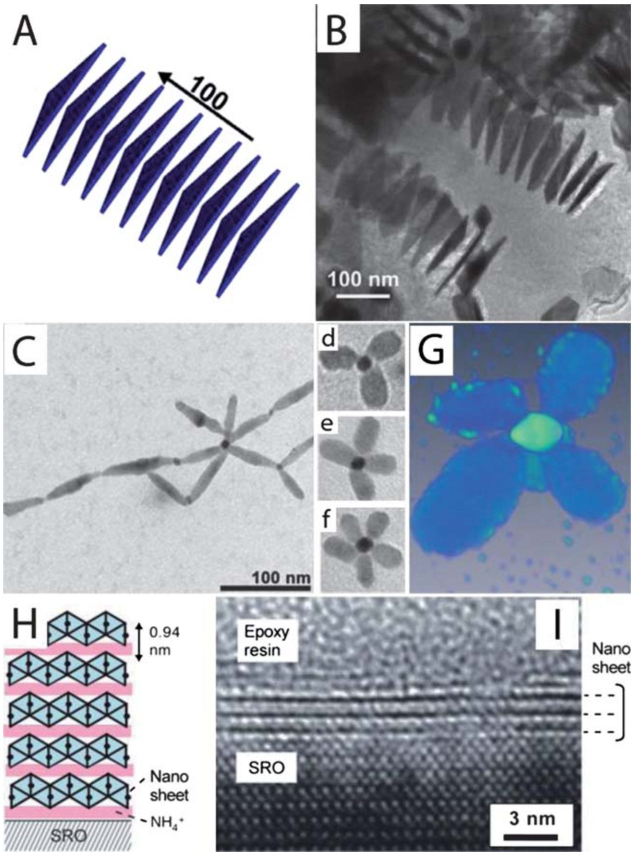

Fig. 4 Chemically induced assemblies of anisotropic NCs: (A and B) schematic drawing and TEM image of ordered arrays of gold nanoprisms formed by DNA hybridization;[106] TEM images of semiconductor nanorods (C) and nanobullets (D–F) assembled by chemical welding through gold domains (see text for discussion) and (G) 3D reconstruction of a flower-like structure based on electron tomography;[11] (H) schematic representation and (I) HRTEM cross-section image of multilayered structure made from titania nanosheets *via* polymer-free LBL assembly.[117] Reproduced with permission from ref. 106 (NPG), 11, 117 (Wiley).

gold domains in solution. Despite the chemical inertness of gold metal in the bulk, small Au nanodomains chemically deposited at the tips of the colloidal heterostructures were found to be very reactive towards coalescence upon addition of small amounts of iodine. Thus, extended networks of tetrapods, chain-like assemblies of nanorods and propeller- and flower-like structures composed of bullet-shaped particles were developed by a simple wet-solution preparation technique (Fig. 4C–G).[11] In these assembly configurations the semiconductor NCs were joined in end-to-end fashion by multi-domain gold welds. Considering the active synthetic development of metal-tipped colloidal NCs[108] and their promising physical properties[109] (*i.e.* synergetic electronic structure and possibility to design charge separation and electron transport pathways) it is expected that this linking strategy has the potential for a broad use in materials design.

Another way to direct the anisotropic assembly of rod-, tetrapod- and multi-branched semiconductor NCs is by destabilization of the capping ligands. Franchini *et al.* utilized small reactive molecules such as acetic acid, hydrazine and trimethylchlorosilane to promote the selective surfactant stripping only from the tips of CdSe@CdTe tetrapods. The resulting "destabilized" tetrapods self-organized into soluble networks through tip-to-tip junctions.[110] It should be noted that tip-to-tip (or end-to-end) assembly of tetrapod-shaped nanoparticles was demonstrated not only for chalcogenide-based tetrapods, but also for other chemical composition structures. For example, Li *et al.* were able to produce multipodal silica particles and decorate their ends either with small Au NCs or tether with thiol (HS-) or formyl functional groups. Such tetrapods were showed to form binary assemblies from complementary units (*i.e.* between Au-decorated and HS-tethered tetrapods) in a reversible fashion.[111]

CISA structures formed from colloidal sheet-like NCs (or nanosheets) are among the most promising anisotropic materials for a diverse range of applications.[112–115] The chemically driven assembly of nanosheets is based on their ability to interact strongly with other nano-objects through van der Waals and electrostatic interactions. The layer-by-layer (LBL) technique is a successful example of how such a strategy can be realized. This technique, originally developed for organic polyelectrolytes, suggests the sequential deposition of oppositely charged layers from solution. Kotov and co-workers demonstrated the formation of layered organic–inorganic composites from montmorillonite clay platelets and polyelectrolytes. This type of composites showed a superior mechanical performance—a reminiscent of both nacre and lamellar bones.[116] The LBL route was also used for the fabrication of high-k dielectric films from titania nanosheets. The ultrathin Ti$_{0.87}$O$_2$ nanosheets (~0.7 nm in thickness) were negatively charged and assembled with alkylammonium-based polycation species to form multilayers (Fig. 4H and I). Such nanofilms have a potential to be employed as gate dielectrics in low dimensional circuits.[117] Similar single-crystalline anatase titania nanosheets, but assembled into hierarchical 3D microspheres, have been shown to be efficient materials for fast and reversible lithium storage.[118] It is interesting to note that the lattice structure of the nanosheets critically influences their assembly. Recent findings of Wang and co-workers suggest that slight structural distortion (below 5%) in individual nanosheets affects their stacking and results in multilayers where sheets are rotated with respect to each other.[119] This study is of general importance because it shows how the inconspicuous structural details of the individual nanocomponents affect the derived assembled mesostructure.

To summarize, the directed assembly of anisotropic NCs is a field of growing interest and its development is closely interwoven and dependent on the progress in the areas of preparation of shape-controlled NCs and colloids[120,121] together with advances in theory and simulations.[122] The latter is especially important for the design of future experimental work due to the challenges posed by anisotropic NCs (*i.e.* inhomogeneous distribution of the electrostatic and chemical potentials across the surface), and requires the realization of new conceptual approaches to drive self-assembly.[123] This study was focused on the shape anisotropy of NCs. Other anisotropies could also arise from the asymmetrical functionalization of isotropic NCs (examples are Janus-, chiral and tethered nanoparticles[124–129]), but those are beyond the scope of this work.

Conclusions

In conclusion, developing new tools to direct the bottom-up self-assembly of inorganic nanoparticles remains a hot research topic. Many opportunities lay ahead on the level of control that can be achieved in the formation of well-designed mesoscale architectures with strong potential for applications. The ability to chemically manipulate the nanoparticle characteristics together with the realization of intuitive chemical strategies to direct their organization can offer a rich set of tools to form new mesoscale functional materials on demand. Here, we reviewed several chemical strategies to drive the self-assembly of spherical and anisotropic structures into one-, two- and three-dimensional anisotropic networks. To better understand the chemistry behind the nanoparticle self-organization we discussed the properties of the inorganic surface and the role of the capping ligands in the self-assembly process. We discussed CISA strategies to form chains, loops and branched networks of spherical and anisotropic nanoparticles based on biomolecular tools, non-covalent and covalent interactions between small organic molecules, ligand destabilization, nanowelding, and layer by layer fabrications of films. The pre-design of the distance and the media between assembled building units as well as the control of the degrees of freedom of the self-organized structures are only few of the advantages that the CISA can offer. The possibilities to manipulate mesoscale structures are continuously increasing with the addition of new tools to the gallery of the already existing ones.

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