

Colloidal Branched Semiconductor Nanocrystals: State of the Art and Perspectives

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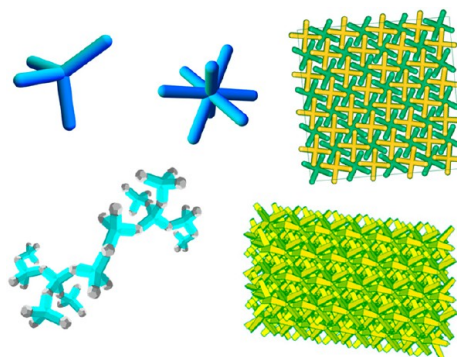
RECEIVED ON AUGUST 9, 2012

CONSPECTUS

Colloidal inorganic nanocrystals are versatile nanoscale building blocks. Advances in their synthesis have yielded nanocrystals with various morphologies including spheres, polyhedra, rods, disks, sheets, wires, and a wide range of branched shapes. Recent developments in chemical methods have allowed the synthesis of colloidal nanocrystals made of sections of different inorganic materials connected together. Many research groups are investigating these nanocrystals' structural and photophysical properties experimentally and theoretically, and many have examined their prospects for commercial applications. Branched nanocrystals, in particular, are gaining attention, in part for their potential applications in solar cells or electronic devices. In this Account, we review recent developments in synthesis and controlled assembly of colloidal branched nanocrystals.

Synthesis of branched nanocrystals builds on previous work with spherical nanocrystals and nanorods, but a unique factor is the need to control the branching event. Multiple arms can branch from a nucleus, or secondary branches can form from a growing arm. Branching can be governed by mechanisms including twinning, crystal splitting, polymorphism, oriented attachment, and others. One of the most relevant parameters is the choice of appropriate surfactant molecules, which can bind selectively to certain crystal facets or can even promote specific crystallographic phases during nucleation and growth. Also, seeded growth approaches recently have allowed great progress in the synthesis of nanocrystals with elaborate shapes. In this approach, nanocrystals with a specified chemical composition, size, shape, crystalline habit, and phase act as seeds on which multiple branches of a second material nucleate and grow. These approaches yield nanostructures with improved homogeneity in distribution of branch length and cross section. Ion exchange reactions allow further manipulation of branched nanocrystals by transforming crystals of one material into crystals with the same size, shape, and anion sublattice but with a new cation. Combining seeded growth with ion exchange provides a method for greatly expanding the library of branched nanocrystals.

Assembly of morphologically complex nanocrystals is evolving in parallel to developments in chemical synthesis. While researchers have made many advances in the past decade in controlled assembly of nanocrystals with simple polyhedral shapes, modeling and experimental realization of ordered superstructures of branched nanocrystals are still in their infancy. In the only case of ordered superstructure reported so far, the assembly proceeds by steps in a hierarchical fashion, in analogy to several examples of assembly found in nature. Meanwhile, disordered assemblies of branched nanocrystals are also interesting and may find applications in various fields.



1. Introduction

Over the last years, the synthesis of colloidal nanocrystals (NCs) has advanced considerably, such that it is now possible in many cases to guide it toward the formation of NCs of

specific sizes and shapes. The unique feature of nanostructures synthesized in solution is that they can be easily manipulated and processed, their surface can be functionalized with various molecules, and they can be organized into

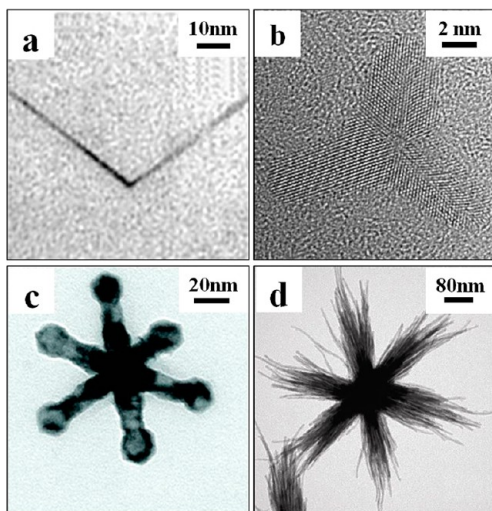


FIGURE 1. Transmission electron microscopy (TEM) images of typical branched NCs. (a) MnS bipod. Reproduced with permission from ref 8. Copyright 2002 American Chemical Society. (b) Palladium tripod. Reproduced with permission from ref 9. Copyright 2009 John Wiley & Sons. (c) MnO hexapod. Reproduced with permission from ref 10. Copyright 2005 American Chemical Society. (d) Highly branched Co_2P NC. Reproduced with permission from ref 11. Copyright 2011 American Chemical Society.

films. Colloidal branched NCs (see examples in Figure 1) are one class of particularly interesting particles, due to their many potential applications.^{1–5} One peculiar aspect of some branched NCs, like tetrapods or octapods, is that they tend to self-align on a substrate, due to their geometry. Such directionality makes these materials interesting for applications, for example, in solar cells and in single NC devices.^{6,7}

This Account will discuss synthetic approaches to colloidal branched NCs, with emphasis on semiconductors. Initial reports in this field addressed the synthesis of colloidal CdTe and CdSe tetrapods^{1,12} and star-shaped PbS and PbSe hexapods.^{13,14} These reports, and following ones, highlighted the importance of specific ligand molecules, for example, alkyl phosphonic acids for cadmium chalcogenide NCs,^{1,12,15} as well as alkyl thiols for PbS NCs,¹³ together with tuning of other parameters (such as temperature and concentrations of the various chemicals) in governing the growth of branched NCs. Further advances in synthesis involved seeding procedures, cation exchange, and the use of more elaborate ligands (for example bifunctional molecules) to create structures with a higher degree of branching and control over the chemical composition and structure of NCs.^{2,15–19} Branched NCs present also interesting questions regarding their assembly: on one hand, a rich variety of ordered superstructures of many different types of particles with shapes ranging from spherical to various

polyhedra have been both realized experimentally and modeled so far. On the other hand, achieving assembly of branched NCs appears to be much more challenging, but some progress is being made in this direction.

2. Overview of the Branching Mechanisms

There are many possible mechanisms that can induce branching in NCs. In semiconductors, a common cause of branching is polymorphism. Other mechanisms involve twinning,^{20,21} oriented attachment,^{10,22} and crystal splitting.^{11,23,24} Metal NCs have also been employed as seeds to synthesize branched NCs.^{25–28} In some cases, understanding what actually caused branching might not be very easy,¹⁰ because uncovering the detailed structure of branched NCs might require a combination of experimental techniques.¹¹ In this section, we will discuss the most common mechanisms that can govern the formation of branched NCs, with practical examples.

Polymorphism arises when a compound can have more than one crystal phase due to the small energy difference between these phases. It is frequent in many II–VI and III–V semiconductors, for which the cubic sphalerite and hexagonal wurtzite crystal phases are favorable at similar temperature and pressure conditions. Tetrapod-shaped NCs, typically made of CdS, CdSe, and CdTe,^{1,12,29} are formed due to polymorphism. Figure 2a displays a TEM image of a CdTe tetrapod,¹ while Figure 2b displays an atomistic model of the tetrapod, consisting of a tetrahedral sphalerite core from which four wurtzite pods depart. To rationalize how these NCs form, one has to imagine that their nucleation occurs in the cubic sphalerite phase, then the growth switches to wurtzite phase, so that four of the original [111] growth directions of the nuclei become the [0001] growth directions of the wurtzite pods.¹ Because the {111} facets of the sphalerite structure are equivalent to the {0001} facets of the wurtzite structure, there is no strain at each core/pod interface. A suitable energy difference between the sphalerite and wurtzite crystal phases appears to be critical to the formation of tetrapods, such that this “switch” can occur easily. Similarly to nanorods and nanowires, the features in the optical absorption spectra of these tetrapods are mainly dictated by the diameter of the pods and not much on their length (Figure 2c,d). Over the years, various refined synthesis approaches to tetrapods have been developed (Figure 2e–h, see also section 3).^{30,31} In the evolution of these branched NCs, a critical role is played by ligand molecules, for example, specific surfactants, which can promote such switching of phases and which affect

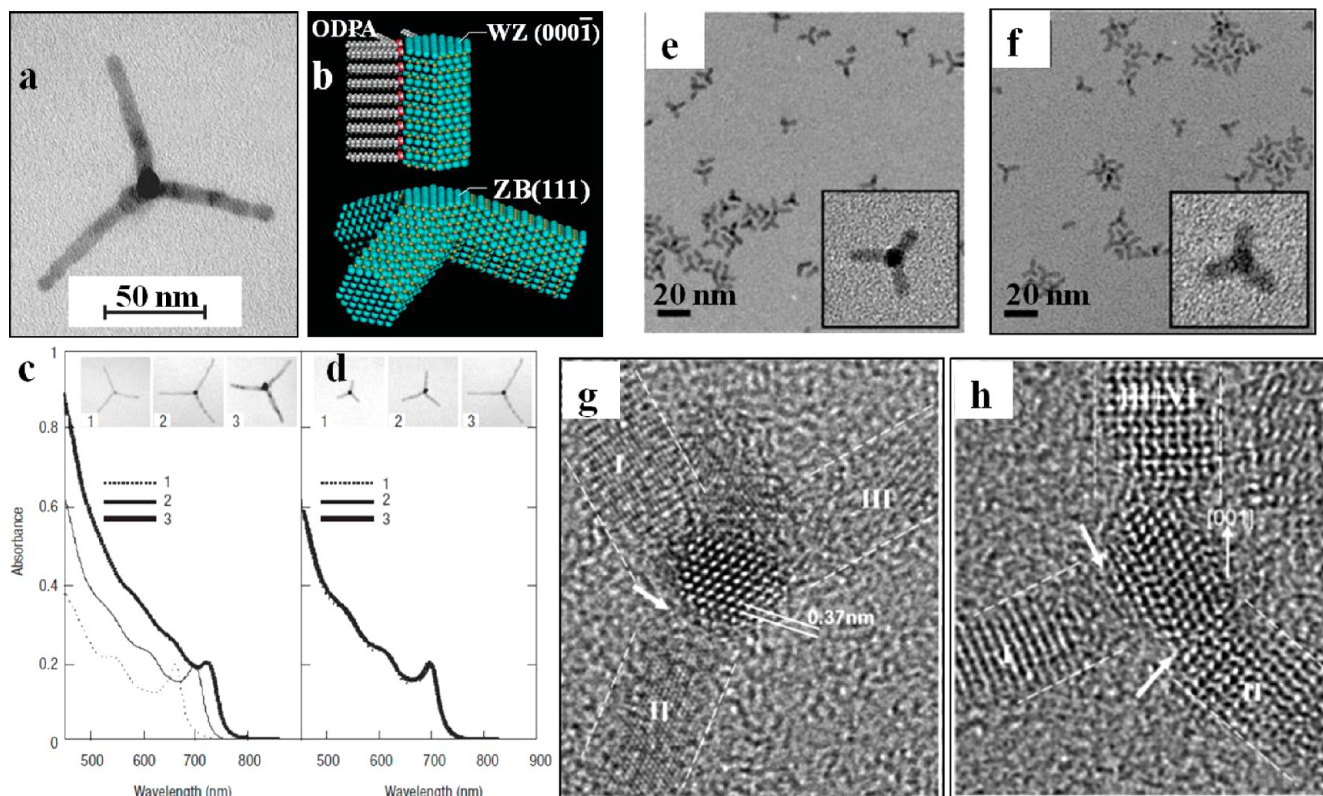


FIGURE 2. (a) TEM image of a CdTe tetrapod. (b) Model of a CdTe tetrapod. (c, d) Optical absorption spectra of a series of CdTe tetrapods with different average pod diameters and lengths. Reproduced with permission from ref 1. Copyright 2003 Nature Publishing Group. (e, f) TEM images of CdSe tetrapods synthesized using cationic surfactants. Reproduced with permission from ref 30. Copyright 2007 John Wiley & Sons. (g, h) HRTEM images of CdSe tetrapods synthesized by tuning the acidity of the reaction medium. Reproduced with permission from ref 31. Copyright 2005 American Chemical Society.

differently the kinetics of growth of the various NCs facets.^{29,16} Temperature also plays an important role in the growth kinetics.³²

Crystals twinning occurs when two distinct crystals share a fraction of the same lattice points in a way that can be described by a symmetry law. When this happens, the two crystalline domains are mutually related by a geometrical operation termed twinning. One possible cause of twinning in NCs is due to aggregation of initially formed particles, which can later develop a preferential growth of certain crystal facets. The driving force in this mechanism is probably arising from an overall balancing of interfacial strain at the twin boundaries and lattice and surface energy of the particle. Twinning plays a major role in the synthesis of many metal and semiconductor NCs, including branched NCs.^{15,20,21,33} One example is TiO₂, for which both the anatase and the rutile phases can exhibit twinning: it was found that the crystal orientation, aggregation and further growth on branch points played a critical role in the formation of anatase TiO₂ branched NCs.^{22,34} Recently, Jun et al. have reported a synthesis of branched NCs of TiO₂ based on

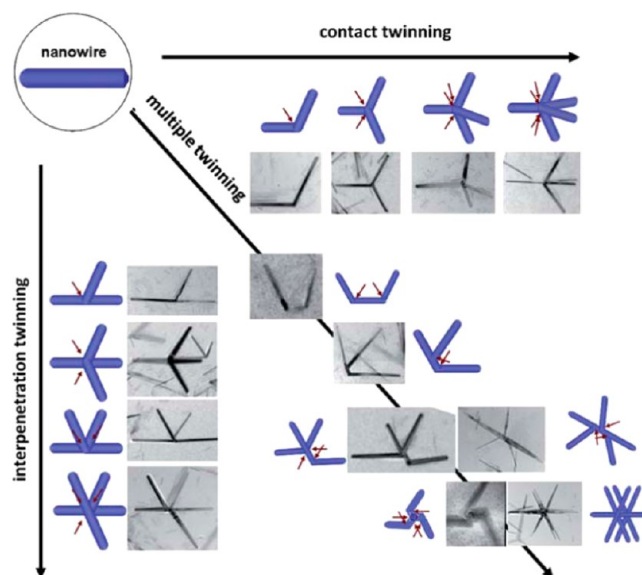


FIGURE 3. A series of branched NCs made of twinned rutile TiO₂. They display two types of twinning: contact twinning and interpenetration twinning. The relative occurrence of the two types of twinning can be controlled by adjusting the synthesis parameters. Reproduced with permission from ref 20. Copyright 2011 Royal Society of Chemistry.

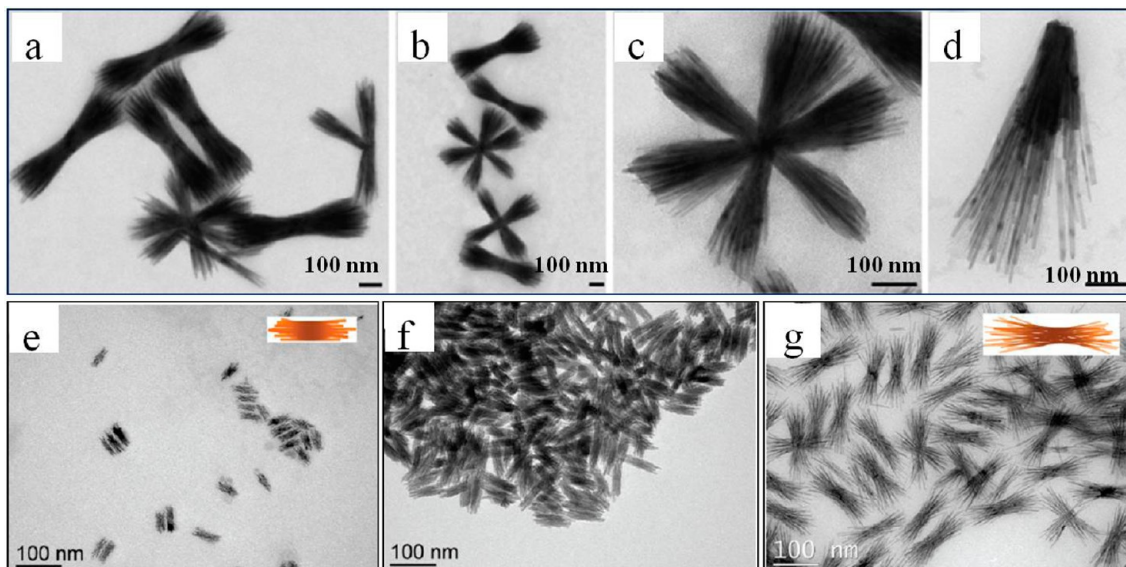


FIGURE 4. TEM images of NCs formed by crystal splitting. (a–d) Branched Bi_2S_3 . Reproduced with permission from ref 23. Copyright 2006 American Chemical Society. (e–g) Co_2P NCs. Reproduced with permission from ref 11. Copyright 2011 American Chemical Society.

twinning (Figure 3).²⁰ By variation of the amount of one component in the synthesis, it was possible to control twinning of the nanowires. The wires grew along the [001] direction and branching occurred upon formation of a (101) twin boundary. Two types of twinning modes were revealed: contact twinning and interpenetration twinning. For contact twinning, the growth direction of the NC changed as a result of twinning, while for interpenetration twinning the growth direction remained the same after twinning. In another work, Ding et al. also demonstrated the synthesis of multipods of rutile TiO_2 via twinning.²¹

Crystal splitting, commonly observed in minerals, may occur due to several reasons, most notably as a consequence of crystal defect resulting from chemical and mechanical factors during the growth process.^{15,23,34} These crystal defects are either formed because of high supersaturations or due to the presence of various impurities, for example, metal ions or biomolecules. In some cases, crystal splitting can be simply the result of multiple twinning as discussed above.³⁴ In other cases, there might be more subtle explanations. As an example, a microstructural study of splitting in biogenic calcite was recently reported.³⁵ Splitting was related to the presence of misaligned domains, with gradients in crystal orientations, which started forming inside the crystals. In some regions of the crystals this misorientation could reach a critical value, which gave rise to crystal splitting, that is, bifurcation.

Alivisatos et al. used a simple colloidal solution method to synthesize highly branched Bi_2S_3 nanostructures, which

resemble the morphology of common minerals.²³ Bi_2S_3 has a strong and tunable splitting ability: by variation of the reaction conditions, Bi_2S_3 nanostructures with different degree of splitting were formed. These included double-sheaf, three to six half-sheaves, and half-sheaf shaped nanoflowers (Figure 4a–c). A similar splitting characteristic has been demonstrated for Fe_2P and Co_2P .^{11,24} Whitmire et al. synthesized branched Fe_2P nanostructures by using single-source molecular precursors.²⁴ They hypothesized that some of the chemicals used in the synthesis could interrupt the crystallization process and promote crystal splitting. Recently, hyperbranched Co_2P NCs were reported by Zhang et al.¹¹ By variation of the synthetic parameters, the size and morphology of the hyperbranched Co_2P could be controlled, from sheaf-like structures to six-arm symmetric star structures (Figure 4e–g). A high density of crystal defects were found at the branching section.

Metal NCs have been widely used as seeds to induce the growth of one-dimensional nanostructures. When particles of metals with a low melting point are used, the growth can be explained via the solution–liquid–solid (SLS) mechanism.³⁶ When noble metal nanoparticles are used, the surface of the particle promotes heterogeneous nucleation of the NC, but there is no diffusion of species inside the metal particle, since this is well below its melting temperature. Metal nanoparticles can also generate branched NCs. Examples are NCs of Ge, PbSe, ZnSe, CdS, CdSe, and CdTe.^{28,33,37,38} When Bi nanoparticles are introduced during the synthesis course, they can induce the formation of

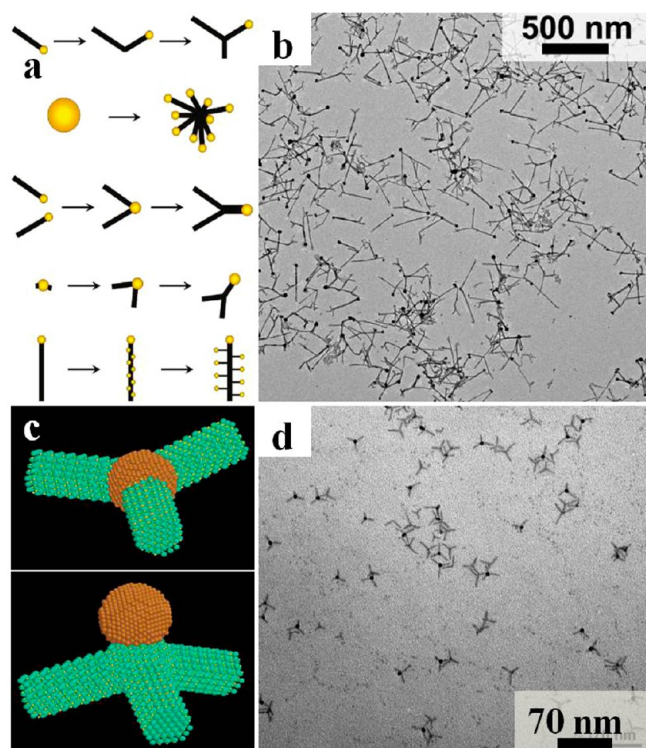


FIGURE 5. (a) Various branching morphologies observed in Ge branched NCs rationalized by the many possible fates of the Bi nanoparticles used as catalysts. (b) TEM image of Ge branched NCs. Reproduced with permission from ref 38. Copyright 2011 American Chemical Society. (c) Schematic models of CdSe nanorods branching out from a gold NC seed. (d) TEM image of CdSe multipods synthesized in the presence of gold seeds. Panels c and d are reproduced with permission from ref 25. Copyright 2006 John Wiley & Sons.

branch points. For example, secondary deposition of Bi NCs onto presynthesized ZnSe nanorods, after which the SLS growth of ZnSe or CdSe was restarted, led to ZnSe or to ZnSe/CdSe branched NCs.²⁸ In a similar synthesis, but of Ge NCs, the various nanostructures were found (Figure 5b) to be dependent on the type of topological interaction between the growing NC and the Bi particles (see Figure 5a).³⁸ Yong et al. reported a series of branched NCs made of CdS, CdSe, PbS, and PbSe.^{26,39} When gold seeds were used for growing CdSe NCs, two types of NCs were found: simple homogeneous CdSe multipods and heteromultipods with the Au particle at the center of the structure (see Figure 5c,d). Metal-induced heterostructured branched NCs can display efficient charge separation at the metal–semiconductor interface, which can be useful for many applications.

In NCs of several materials, the formation of dendritic, that is, fractal-like shapes, is often observed. Typical examples are Ag⁴⁰ and Pt NCs.⁴¹ For these dendrites, the highly irregular shape of the particles is often explained by the templating effect of the surfactants used in the synthesis.

Other general mechanisms of formation of dendritic NCs are based on reaction conditions typically observed for bulk dendrites, for example, conditions in which the growth is governed by the so-called diffusion-limited aggregation of random moving nuclei, whereby various degrees of supersaturation promote different aggregation patterns.^{42,43} Dendritic shapes can be even the result of oriented attachment of smaller NCs.⁴⁴ Branched NCs of TiO₂, MnO, and PbSe have been synthesized via oriented attachment.^{10,22,45} Especially in the case of PbSe, NCs with different morphologies, including star-shape, radially branched nanowires, and zigzag nanowires were reported.⁴⁵

Seeded growth approaches use small nanoparticle seeds as additives in the reaction mixture to promote the growth of branches/pods in a controlled way. Due to the relatively larger activation energy of the homogeneous nucleation with respect to heterogeneous nucleation, it is more favorable for NCs to nucleate heterogeneously on the surface of the seeds than as isolated entities in solution. Based on these approaches, semiconductor nanorods with narrow distributions of lengths were synthesized by us and by other groups.^{16,17} The case of tetrapods is emblematic because traditionally their synthesis relied on conditions in which nucleation occurs in one phase and growth occurs in another phase, which might be difficult to reproduce. Many recent syntheses of tetrapods exploited instead seeded growth: first, NCs in the sphalerite phase (CdSe, ZnTe, and CdTe) were prepared, and then they were used as seeds for growing tetrapods. In the second step, conditions can be tuned such that pods grow exclusively on top of the seeds. Examples of “seed-grown” tetrapods are CdSe/CdTe, ZnTe/CdTe, ZnTe/CdS, ZnTe/CdSe, and CdSe/CdS (Figure 6).^{2,17} These heterostructures also have interesting optical properties. For example, CdSe/CdTe exhibit a narrow photoluminescence (PL) signal from the CdSe core region but also a broader PL signal at lower energy due a type-II recombination of carriers that are spatially separated at the core–pod interface.² CdSe/CdS tetrapods display high PL quantum yield in the visible range, similarly to the case of CdSe/CdS dot/rod NCs, indicating a good passivation of the CdSe core.¹⁷ Also, dual emission in CdSe/CdS tetrapods and nanorods (i.e., both from the CdSe and from the CdS regions) was recently observed.^{46,47}

One additional requisite for obtaining high yields of tetrapods is that the seed remains in its cubic phase during the synthesis. Huang et al. found that short alkyl chain phosphonic acids improve the phase stability of the seed and increase the yield of tetrapods.⁴⁸ It is also possible to synthesize tetrapods that are entirely in the cubic sphalerite

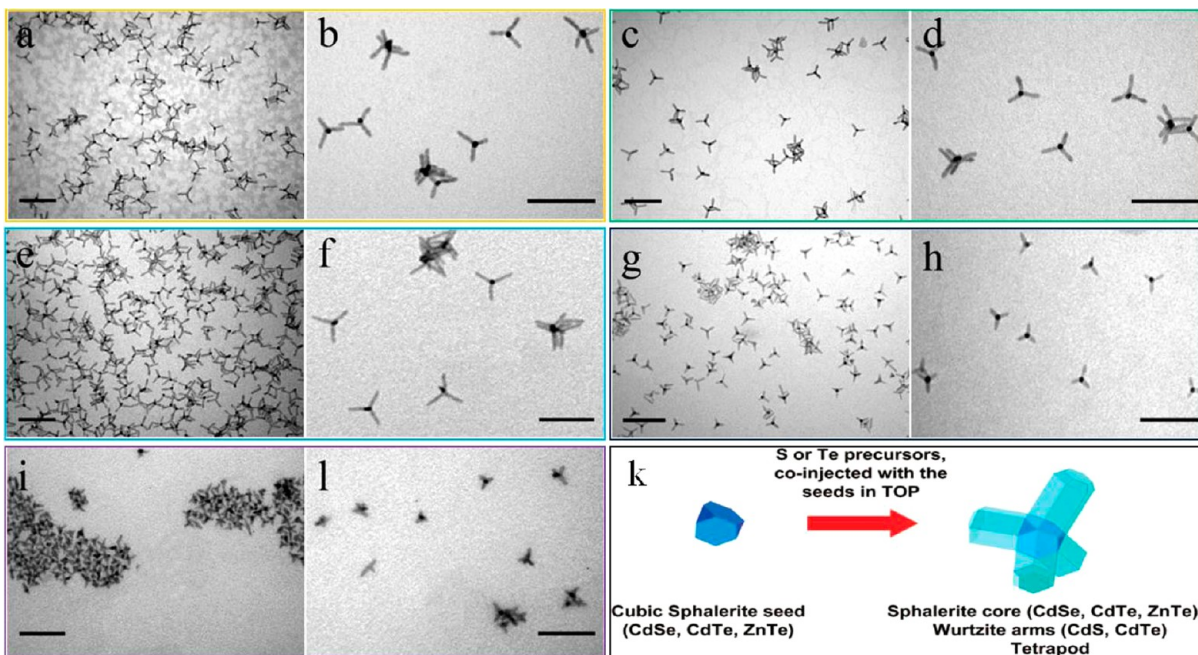


FIGURE 6. TEM images of tetrapod-shaped NCs (denoted as core/arm) prepared by seeded growth. (a, b) CdTe/CdTe, (c, d) CdSe/CdTe, (e, f) ZnTe/CdTe, (g, h) ZnTe/CdS, and (i, l) ZnTe/CdSe. All scale bars are 100 nm long. (k) Sketch of the seeded growth of tetrapods. Reproduced with permission from ref 2. Copyright 2009 American Chemical Society.

phase.⁴⁹ Simply, the growth of either wurtzite or sphalerite pods can be decided by using different ligands for the synthesis.⁴⁹ Zheng et al. have shown that the region at the interface between the central core and the pods in CdSe/ZnS tetrapods has an alloy composition,⁵⁰ which helps to reduce the strain at that region. Recent reports have demonstrated control over the shape of the pods.⁵¹

The influence of size of the seeds on the growth of NCs has been investigated.⁵² For cubic CdTe seeds, Zhong et al. discovered that increasing their size enhanced their tendency to yield branched nanostructures, because the morphologies of the final NCs evolved from nanorods to tripods to tetrapods.⁵³ Our group demonstrated that large (10–15 nm in diameter) CdSe sphalerite nanoparticle seeds with octahedral shape induce the formation of octapods.⁵⁴ Such large seeds were obtained from Cu_{2-x}Se NCs by exchanging Cu^+ ions with Cd^{2+} ions. The transformation preserved the shape and the size of the starting Cu_{2-x}Se NCs (Figure 7). These CdSe seeds had all of their eight $\{111\}$ facets well developed, and on top of each of these facets a CdS pod was grown. It appears that to grow octapods seeds of both appropriate size and shape are needed, such that each of their eight $\{111\}$ facets can promote the growth of a pod. Recent work from our group has shown that under appropriate conditions the octapod is only an intermediate shape, which evolves to a tetrapod over time.⁵⁵

More complex NCs can be exploited as seeds. Zhong et al. synthesized CdTe/CdSe branched NCs by using CdTe tetrapods as seeds to induce the growth of CdSe on their tips.⁵⁶ Milliron et al. prepared various heterostructures starting from either CdS nanorods, CdSe nanorods, or CdSe tetrapods as seeds.¹⁹ Also, nanostructures of IV–VI semiconductors, such as the PbTe/PbSe core/shell six-armed nanostars, have been synthesized via seeded growth.⁵⁷ The nanostar-like crystals can be seen as made by a truncated octahedron (the core) and six symmetric arms grown from the corresponding six $\{001\}$ facets of the core, each in the $[100]$ direction.

In cation exchange, the sublattice of cations in ionic NCs can be partially or totally replaced with a new sublattice of other cations, while the anion sublattice remains practically unchanged.^{58,59} In many studies on cation exchange reactions performed on NCs, it was found that they can preserve the size and the shape of the starting NCs and they even produce particles with metastable crystal phases.^{58,59} Cation exchange reactions can be exploited to prepare NCs that so far have been difficult to make by conventional synthetic methods.⁶⁰ Only a few examples of branched NCs obtained by cation exchange have been demonstrated so far. Son et al. reported the transformation from CdTe tetrapods to Ag_2Te tetrapods by exchanging Cd^{2+} with Ag^+ and then their recovery to CdTe tetrapods via the reverse reaction.⁶⁰ Recently, our group exploited exchange of Cd^{2+} with Cu^+ to

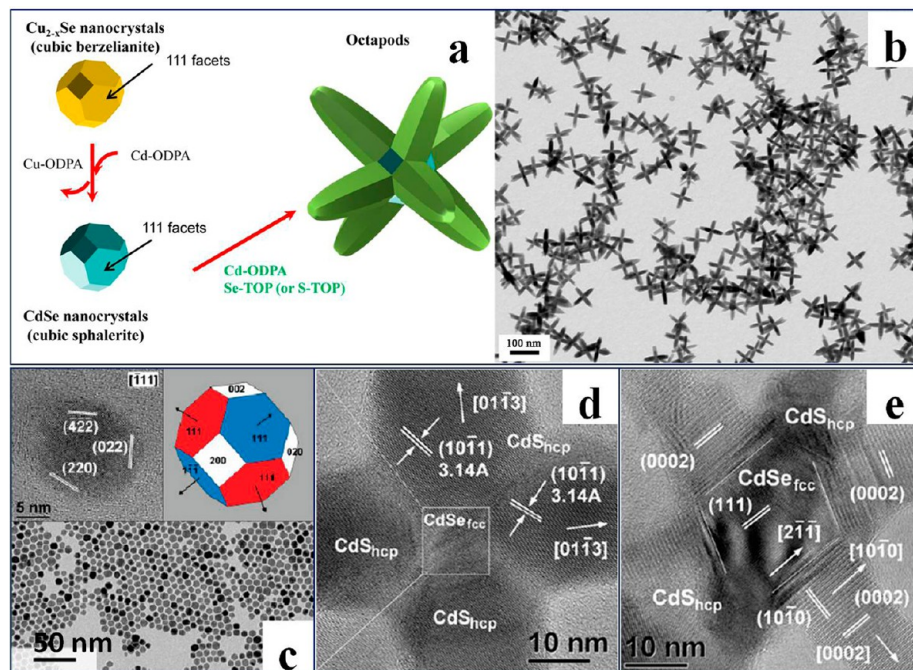


FIGURE 7. (a) Mechanism of formation of octapods and relative TEM images. (b) Low magnification TEM image of several octapods. (c) TEM and HRTEM images of the Cu_{2-x}Se seeds, and a schematic model of the crystal habit; (d, e) HRTEM images of the CdSe/CdS octapods acquired at different zone axes of the CdSe seeds. Reproduced with permission from ref 54. Copyright 2010 American Chemical Society.

transform CdSe/CdS octapods into $\text{Cu}_2\text{Se}/\text{Cu}_2\text{S}$ octapods but also into intermediate structures.¹⁸ The process was controlled by regulating the amount of copper precursor added. The reaction started at the tips of the octapods; thus a series of intermediate heterostructures could be isolated in which the outer sections of the pods were made of hexagonal chalcocite Cu_2S , while the inner pod sections were still hexagonal wurtzite CdS. When the exchange was complete, the pods were transformed entirely to Cu_2S , while the central region became cubic Cu_2Se . In general, cation exchange reactions represent a powerful tool for expanding the so far limited range of branched NCs compositions. Since they can be performed also in assemblies of NCs^{4, 61} without perturbing them, the potential for further developments in this direction is noteworthy.

3. Assembly

Considerable progress has been made so far in controlling and modeling the self-organization of colloidal particles in ordered three-dimensional structures.⁶² A recent computational work has catalogued the assembly behavior of polyhedral particles of many possible shapes into close-packed superstructures.⁶³ One of the outcomes of the study was that a large set of polyhedra NCs might not form crystalline close-packed superstructures due to steric restrictions arising from their morphology. In these cases, when formation of

superstructures is attempted by slowly increasing the volume fraction of particles (which is equivalent to gradually increasing the volume fraction of NCs, for example, by slow evaporation), these can be trapped into locally jammed structures, with each particle limiting the movement of its neighbors. A similar limitation would apply to branched NCs. On the other hand, this does not rule out the possibility for branched NCs to form ordered superstructures. Our group reported indeed the first example of ordered superstructures of branched NCs using octapod-shaped NCs as building blocks.⁴ It was found that the particles initially self-organized into linear chains, as soon as the octapod–octapod interactions became stronger than octapod–solvent interactions. When two octapods approach one another, they can reach an “interlocked” configuration if one of the two is appropriately rotated with respect to the other. This configuration maximizes the contact area between the two octapods. Any other octapod willing to join the dimer, can do it only from the two sides of the dimer for which this interlocked configuration is still possible, yielding chains of interlocked octapods (Figure 8b–d). These chains then interacted with each other and self-zipped into ordered 3D superstructures (Figure 8e,f). This type of hierarchical organization is achieved by slowly decreasing the stability of the octapods in solution. What is also remarkable is that the initial concentration of NCs was far lower than in the more traditional

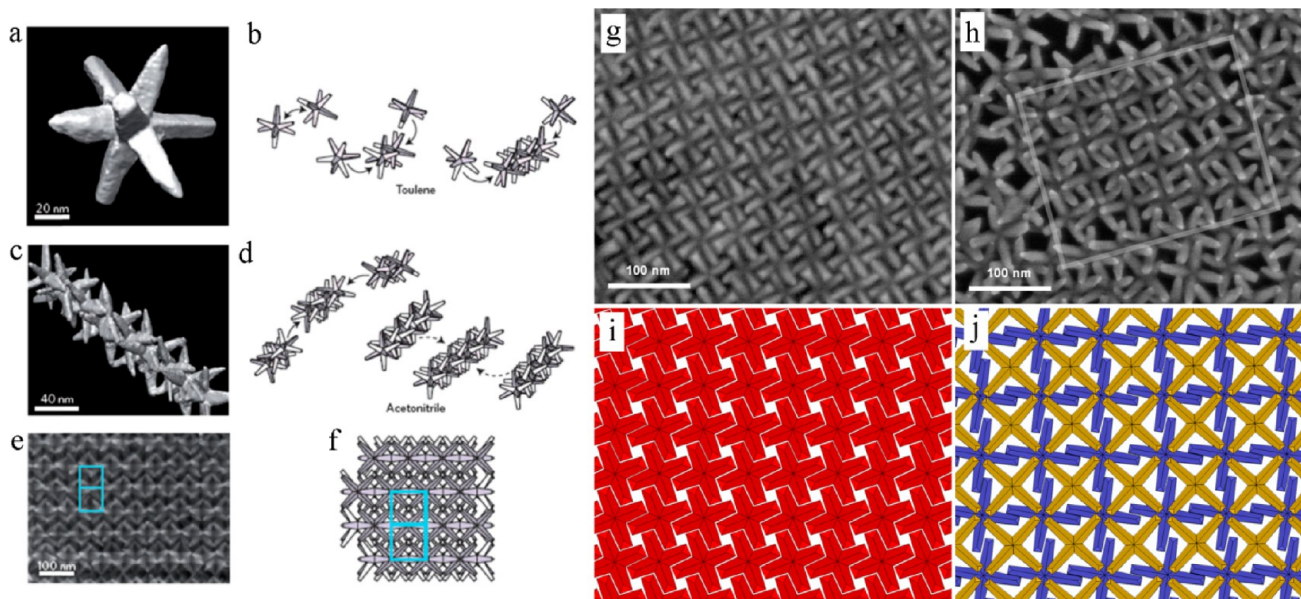


FIGURE 8. (a–f) Various steps of the hierarchical assembly of octapods in solution by modification of the NC solubility. Reproduced with permission from ref 4. Copyright 2011 Nature Publishing Group. (g–j) Assembly of octapods on a flat substrate following solvent evaporation: (g, i) simple square lattices; (h, j) binary square lattices. Reproduced with permission from ref 64. Copyright 2012 American Chemical Society.

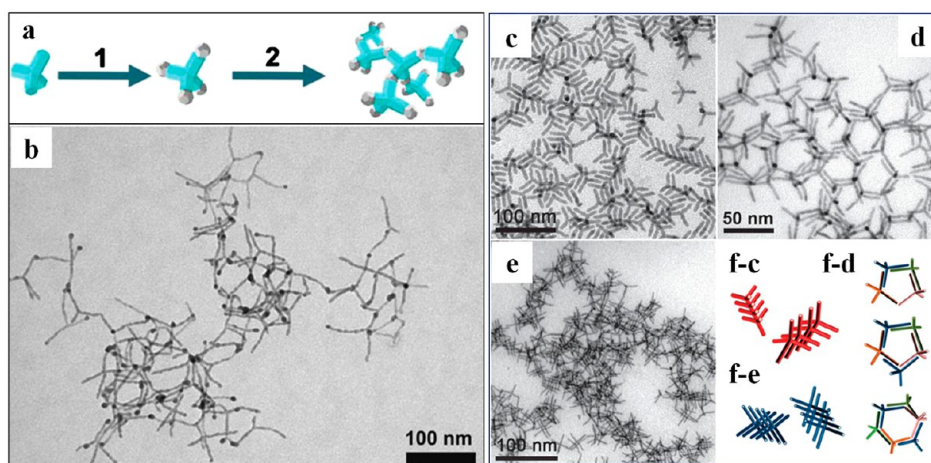


FIGURE 9. (a) Sketch of self-assembly of tetrapods by the nanowelding approach and (b) TEM image of a representative assembly. Reproduced with permission from ref 66. Copyright 2009 John Wiley & Sons. (c–e) TEM images of typical assemblies of ZnTe/CdTe tetrapods and (f) models of the various assembly motifs that were found experimentally. Reproduced with permission from ref 65. Copyright 2011 Royal Society of Chemistry.

conditions of nanoparticle assembly by slow solvent evaporation.

Recent work by our group has shown that upon deposition of a solution of octapods on a flat substrate and subsequent solvent evaporation, octapods are preferentially assembled into two-dimensional square lattices (either simple lattices or binary lattices).⁶⁴ Here, the substrate forces the NCs to touch it with four pods and therefore limits their free rotation in space. Consequently, octapods cannot form interlocked structures.

One can expect that, in principle, branched NCs can display a rich assembly behavior based on their shape. In a recent work, we have shown how the addition of various surfactants and polymers in a solution of tetrapods can induce a partially controlled aggregation of the tetrapods into various structures with a certain degree of local order (Figure 9c–f).⁶⁵ Here, the tendency of the pods of neighboring tetrapods is to be parallel to each other, in order to maximize interparticle interaction. It is likely that also the assembly of tetrapods into ordered superstructures will be

improved in the future, as soon as more suitable experimental conditions are identified.

Other assembly schemes for branched NCs do not involve ordered structures as a final goal: self-assembly of NCs by a “nanowelding” approach, was introduced recently by us.⁶⁶ This was achieved first by growing Au domains on the tips of the NCs and then by inducing coalescence of the Au domains. This yielded disordered 3D networks of tetrapods welded at their tips by gold nanoparticles (Figure 9a,b).

4. Conclusions and Perspectives

In this Account, we have reviewed the recent developments in the synthetic approaches of colloidal branched NCs as well as the current strategies for their assembly. We focused on different types of mechanisms responsible for the formation of branched NC, and discussed the most important of them. We believe that an in-depth understanding of the growth mechanisms will be of critical benefit for the fabrication of high-quality branched NCs. In this scenario, the interesting combination of the seeded growth approach followed by partial or total or even multiple cation exchange reactions could greatly expand the library of available branched NCs. Their organization in mesostructures, possibly over large areas, is of great interest not only because of the potential intrinsic properties of the assemblies but also because of the fundamental aspect of the organization of anisotropic structures. We are still at the beginning of our attempts to break the code of assembly commands programmed in the morphological characteristics of a structurally complex particle. In principle, deciphering this code will allow us to design and fabricate a large variety of new artificial solids.

This work was supported by the EU FP7 ERC Grant NANO-ARCH (contract no. 240111). L.M. and A.G.K. acknowledge the Royal Society for an International Joint Project Grant.

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FOOTNOTES

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