

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/280646369>

Occurrence of Polytypism in Compound Colloidal Metal Chalcogenide Nanocrystals, Opportunities, and Challenges

ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · JULY 2015

Impact Factor: 7.46 · DOI: 10.1021/acs.jpclett.5b01311

READS

27

2 AUTHORS, INCLUDING:



Shalini Singh

University of Limerick

14 PUBLICATIONS 183 CITATIONS

SEE PROFILE

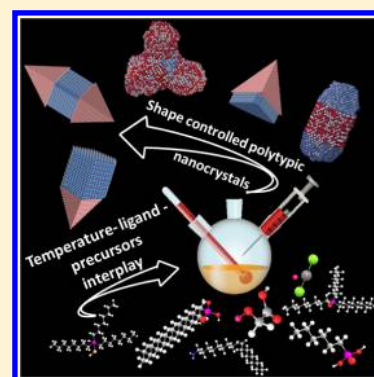
Occurrence of Polytypism in Compound Colloidal Metal Chalcogenide Nanocrystals, Opportunities, and Challenges

Shalini Singh^{†,‡} and Kevin M. Ryan^{*,†,‡}

[†]Materials and Surface Science Institute, University of Limerick, Limerick, Ireland

[‡]Department of Chemical and Environmental Sciences, University of Limerick, Limerick, Ireland

ABSTRACT: This Perspective will look at the occurrence of polytypism in colloidal nanocrystals of metal chalcogenides. The low energy barrier between growth in wurtzite and zincblende crystal phases allows the occurrence of both in a single particle which has a dramatic influence on shape control. To date, various strategies have been employed to understand and control this phenomenon leading to a range of particle shapes across a wide range of semiconductor compositions from the archetypal cadmium selenide to the more recently studied compound copper chalcogenide nanocrystals such as dicopper–zinc–tin tetrasulfide and copper indium gallium selenide systems. The Perspective will also look at the control factors for polytypism in colloidal nanocrystals and the impact of polytypism on end-use applications.



Polytypism can be defined as the occurrence of two crystal polymorphic forms within the same particle.¹ It is generally prevalent in tetrahedrally coordinated IV, III–V, and II–VI semiconductors crystals due to large atom stacking freedom, among which hexagonal wurtzite (WZ) and cubic zincblende (ZB) are two very commonly observed polymorphs.² The (111) plane of the cubic ZB lattice structure can interface well with the (002) plane of the hexagonal WZ structure, allowing for ease of transition between growth in either phase to create polytypes.³ This allows for the nucleation of a particle in one crystal phase with the subsequent transition to growth in another crystal phase leading to shape morphologies that are not possible in single crystal systems.

For example, branched 3-D morphologies are obtained when the nucleation takes place in ZB with subsequent growth in WZ (Figure 1). The faceting of the ZB seed is such that it has eight {111} crystalline facets that each can serve as nucleation points for subsequent transition to growth of WZ. The formation of tetrapod nanocrystals are obtained when the four {111} ZB facets (more reactive facets compared to other four {111} ZB facets) allow the epitaxial growth of wurtzite pods. Octapod nanocrystals are obtained when all the eight {111} ZB facets serve as nucleation facets for epitaxial growth of WZ pods under suitable conditions (Figure 1a). Branched polytypes of this form with nucleation in ZB and then subsequent growth in WZ have been observed with, tetrapods of CdSe,^{5–7} CdTe,^{7–9} CdS,^{10,11} ZnSe,^{12,13} ZnTe,¹⁴ and multipods of CdSe/CdS^{3,5,15} and CdSe/CdTe.³

Polytypes arising from nucleation in the WZ phase with subsequent growth in ZB are always linear 1-D structures.¹⁶ In WZ, there are only two opposite {002} facets that can allow transition to epitaxial growth of ZB tips. Additionally, the reactivity of + (002) facet differs from that of – (002) facet which

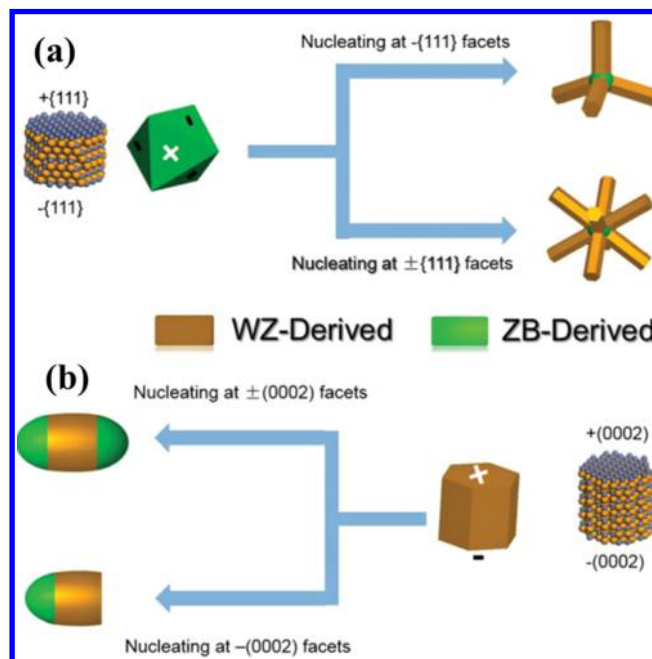


Figure 1. Schematic illustration of the polytypic nanocrystal growth with different morphology. Adapted with permission from ref 4. Copyright 2014, Royal Society of Chemistry.

gives access to localize the ZB tip selectively on one or both ends of the WZ core (Figure 1b).⁴

Received: June 19, 2015

Accepted: July 30, 2015

The most common route to polytypic nanocrystals is the colloidal hot-injection method as it allows separation of cationic and anionic species until nucleation (injection) and facilitates different temperatures for nucleation and growth.

The most common route to polytypic nanocrystals is the colloidal hot-injection method as it allows separation of cationic and anionic species until nucleation (injection) and facilitates different temperatures for nucleation and growth. This allows nucleation in the kinetically stable phase and growth in the thermodynamically stable phase with increasing temperature. Consequently, the tetrapod polytypes are more commonly found in II–VI nanocrystals where ZB is the metastable nucleating seed, whereas linear morphologies are common in I–III–VI nanocrystals and their derivatives where the wurtzite seed is metastable.^{4,16}

This Perspective will investigate the occurrence of polytypism in binary, ternary, and quaternary metal chalcogenide nanocrystals, the challenges in controlling the morphology of polytypic nanocrystals and effect of structural difference within a single nanocrystal on the intrinsic properties. We will also outline the exploitation of these nanostructures as single nanocrystals or assembled layers in real life applications such as hybrid organic–inorganic photovoltaics, lithographically patterned devices, probe tips for high resolution atomic force microscopy, and thermoelectrics.

Binary II–VI Semiconductor Polytypic Nanocrystals. In the II–VI semiconductor nanocrystal system, Alivisatos and co-workers demonstrated complete control over the shape of CdSe nanocrystals using a colloidal approach in the early 2000s.⁶ They varied three fundamental reaction parameters: ratio of the surfactant in the growth solution (hexylphosphonic acid (HPA)/triethylphosphine oxide (TOPO)), volume of initial injection, and time dependence of monomer concentration. Although a major observation of this work was the discovery that different combinations of surfactants can speed up or slow down growth rates along certain crystal directions to affect shape control in a single crystal system, they also observed more complex tetrapod shapes that could only arise from polytypism. Initially, this was observed as a random event sometimes aided by unintentional impurities in different batches of phosphonic acid surfactants. The frequency of occurrence of random polytypism was also observed to be greater with CdTe in comparison to their sulfur or selenium analogues.^{9,17} In the very first studies of polytypic morphologies in II–VI inorganic materials, the serendipitous occurrence of branched nanocrystals was considered to be a result of difference in the growth rate of different crystal facets as a function of time.⁶

In a seminal work on high yield synthesis of CdTe polytypic tetrapods by Manna et al., independent tuning of the pod length and diameter was achieved by manipulation of growth kinetics.⁸ CdTe have an energy difference between ZB and WZ phases large enough that at elevated temperatures, (10 meV) high quality of WZ growth is preferred with selective nucleation in ZB structure. Using long alkyl chain phosphonic acid (octadecyl phosphonic acid (ODPA)) as the ligand selectively

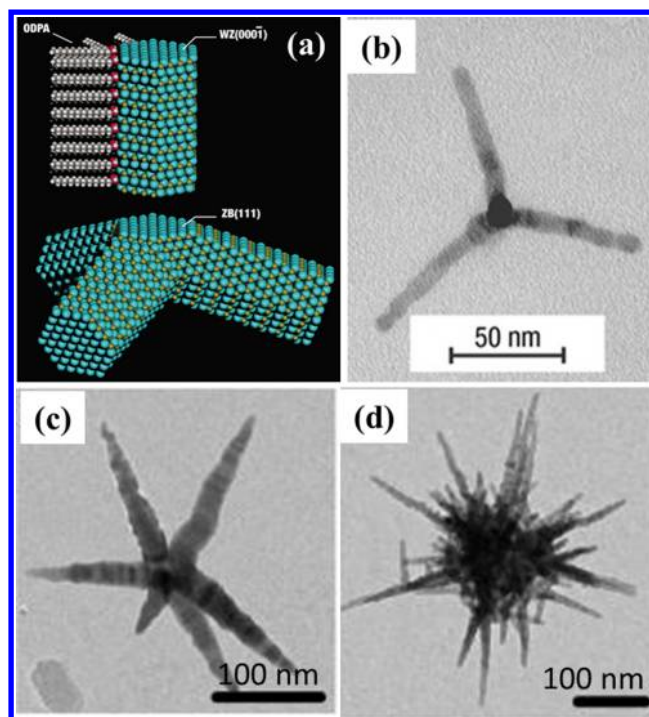


Figure 2. II–VI polytypic nanocrystals (a) Crystal model of CdTe tetrapod. (b) Transmission electron microscope (TEM) image of a CdTe tetrapod. (c) High resolution TEM (HRTEM) image of CdSe multipod nanocrystals synthesized by using monofunctional phosphonic acids (propylphosphonic acid and tetradecylphosphonic acid). (d) HRTEM image of CdSe hyperbranched nanocrystals synthesized by using bifunctional phosphonic acid (2-carboxyethylphosphonic acid) with tetradecylphosphonic acid. Reprinted with permission from refs 8 and 7. Copyright 2003, Nature Publishing Group, and copyright 2005, American Chemical Society.

stabilizes the nonpolar lateral facets of the CdTe WZ phase which are not equivalent to the CdTe ZB phase (Figure 2a,b). Presence of excess ODPA per Cd^{2+} (lower Cd/ODPA ratio) decreases the reactivity of the Cd precursor and slows down the growth rate resulting into larger diameters of the pods. On the other hand, a high Cd/Te ratio increases the growth rate and results into longer pod growth in WZ phase. The formation and stability of CdE (E = Te, Se, S) tetrapod structures were studied intensively by different research groups to determine the effect of various ligands, monomer reactivity and temperature on the polytypic nanocrystal growth in binary systems.^{6,7,9,10,18–23} Each of these factors is interdependent, yet interesting observations on the growth mechanism becomes apparent if one is used as a control factor. Take for example temperature: Cheon et al. showed that the number of WZ pods growing from the (111) ZB planes in CdS could be increased from one to four by reducing the temperature of growth from 300 to 120 °C, with all other reagents in their synthetic protocol remaining constant.¹¹ The thermodynamic influence on the occurrence of polytypism was best observed by Huis et al., who showed that post-synthetic transformation of uncapped (ligand-free) spherical zincblende CdSe seeds into polytypic tetrapods or octapods having WZ pods by annealing the samples at high temperature.²¹ The ZB to WZ local structural transition starts from the outermost layers proceeding into the inner layers as predicted by molecular dynamic simulations and confirmed by in situ TEM. In a colloidal system, additives such as quaternary ammonium salts in addition to the phosphonic ligands²² have

also shown to induce branching during growth in good agreement with similar observations with respect to short chain phosphonic acid impurities with CdE.²⁴ Control of such factors that allow for branching can be exploited to give hyperbranched (more than four pod) nanocrystals under optimum conditions. Kanaras et al. showed that low concentration of the chalcogenide precursor, presence of short alkyl chain, and bifunctional phosphonic ligands as surfactants allow the formation of snowflake-like polytypic structures by growth of multi-WZ pods from a ZB derived core (Figure 2c,d).⁷

To date, polytypic zinc chalcogenides have shown higher yield when synthesized by thermochemical methods based on evaporation and condensation vapor processes^{12,25} or solvothermal processes.²⁶ In colloidal approaches, precursor reactivity have been investigated and tuning of supersaturation conditions to provide thermodynamic control of the growth mode and enable switching between the ZB and WZ structures.^{13,14} *I₂–III–VI Semiconductor Polytypic Nanocrystals.* Similar to the II–VI binary and ternary semiconductor nanocrystals, I–III–VI semiconductors such as CuInS₂ (CIS), CuInSe₂ (CISE), and CuInGaSe₂ (CIGSe) are considered theoretically to be derived from the binary ZnSe through replacing part of Zn atoms by Cu, In, and Ga atoms.²⁷ The binary ZnSe have the ZB and WZ structures; therefore, ternary and quaternary nanocrystals have the corresponding ZB-derived and WZ-derived structures. The most stable states are the ZB-derived phases; however, by manipulating the reaction kinetics, metastable WZ phases can also be formed.²⁸ Furthermore, unexpected polytypism also can be observed in these systems during the solution-based colloidal synthesis. The first example of polytypism in these multinary systems was randomly discovered by Korgel et al.²⁹ during CuInS₂ nanodisks synthesis, where the WZ phase interfaces with significant chalcopyrite (CH) domains across (002)_{WZ}/(112)_{CH} stacking faults. Later, different researchers found that during the colloidal synthesis, at lower temperatures, the metastable wurtzite form of CuInS₂ occurs as nanoplates, but as the number of metal cations decrease with further progression of the reaction, WZ–ZB polytypism occurs in the system.^{30,31} Furthermore, partial or complete substitution of Ga or Fe in the crystal lattice of CuInS₂ to form CuInGaS₂ (CIGS), CuGaS₂, or CuInFeS₂ also results into the occurrence of WZ–ZB or WZ–CH polytypism.^{32–35} However, formation of branched morphologies or 1-D linear structures were not reported in Cu–In–Ga–S/Se systems.

I₂–II–IV–VI₄ Semiconductor Polytypic Nanocrystals. Separation of nucleation and growth events into two different phases to

Separation of nucleation and growth events into two different phases to form branched polytypic nanocrystals is much more difficult in the ternary and quaternary compounds than in the binary compounds, as it involves many more reaction parameters to balance.

form branched polytypic nanocrystals is much more difficult in the ternary and quaternary compounds than in the binary compounds, as it involves many more reaction parameters to

balance. We reported, for the first time, formation of tetrapods in ternary Cu₂SnSe₃ (CTS) nanocrystals showing the possibility of complex 3-D structures in the case of multinary semiconductors (Figure 3a–b).³⁶ The high temperature injection

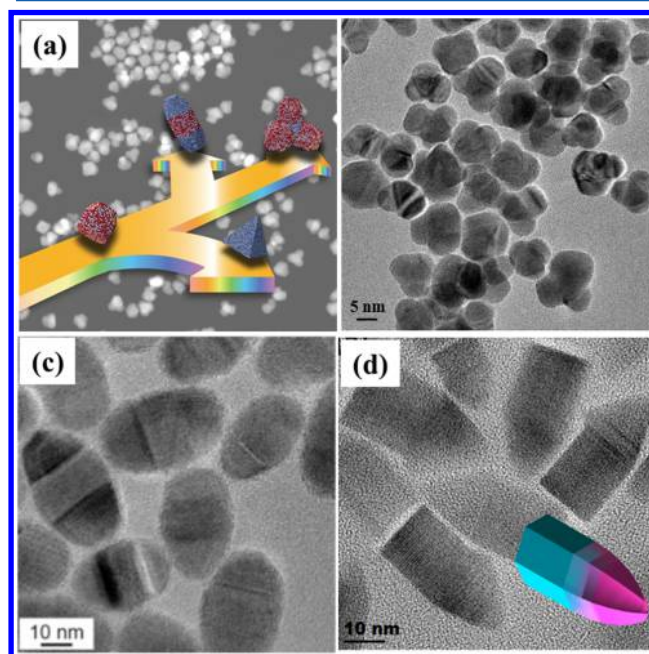


Figure 3. (a) Cover art showing a 3D model of different nanoparticles type formed, hexagonal, cubic, linear heterostructure, and tetrapod, highlighting the ability to synthetically control the formation of each in a single system. (b) TEM image of Cu₂SnSe₃ tetrapods. (c) TEM image of Cu₂SnSe₃ linear heterostructures. (d) TEM image of pencil shaped Cu₂ZnSnS₄ (CZTS) polytypic nanocrystals. Adapted from ref 36–38. Copyright 2013 and 2014, American Chemical Society. Copyright 2015, The Royal Society of Chemistry.

(310 °C) favored the nucleation in ZB and subsequent growth at a slightly lower temperature (295 °C) lead to the formation of WZ arms.³⁷ The interface between the ZB and the WZ phases shared the same planes as they do in the case of CdTe or CdSe. The polytypism can be tuned in both 3-D branched shape and 1-D rod shapes by judicious selection of different precursors, ligands, and reaction temperature. The formation of linear heterostructures (1-D nanocrystals) requires the nucleation at low temperatures to facilitate formation of the metastable WZ seed (Figure 3c,d). Temperature ramp with further progression of the reaction leads to the epitaxial growth of ZB derived structure on the two (002) facets of the wurtzite seed (Figure 4c). The reactivity coefficients of the metal precursors and their compatibility with the ligands have a huge impact on the formation of single or separate domains in nanocrystals.

Formation of linearly arranged ZB/WZ/ZB polytypic CZTSSe nanocrystals in rugby-ball shape was also shown by Yu and co-workers.¹⁶ These nanocrystals were found to have two possible typical sequences at the WZ–ZB interface, that is, ...ABC/AB...AB/CBA... and ...ABC/AB...AB/ABC.... The first case reflects that the central WZ-derived domain acts as a twinning plane of ZB-derived structure, whereas in the latter case, it looks like that one ZB-derived nanoparticle is separated by a WZ-derived domain. When the wurtzite plate acts as seed both {0002}WZ facets can serve as nucleation facets for the epitaxial growth of ZB pods. Additionally, due to the difference between the reactivity of +(002)WZ and –(002)WZ facet, it is

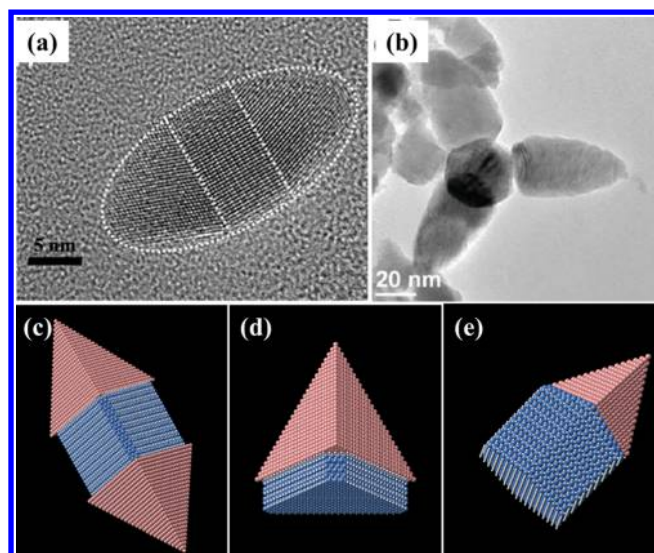


Figure 4. (a) HR-TEM images of rugby-ball shaped polytypic CZTSSe nanocrystals with a central wurtzite core and zincblende ends. (b) HR-TEM image $\text{Cu}_2\text{Cd}_4\text{SnSe}_4$ polypods with zincblende derived core and wurtzite pods. (c–e) 3-D crystal models of the ellipsoidal, arrow-shaped and bullet shaped polytypic CZTSSe nanocrystals with wurtzite core and zincblende derived tips. Reproduced with permission from refs 16, 39, and 40. Copyright 2012, Nature Publishing Group, and 2014, American Chemical Society.

possible to selectively grow one or two ZB structure from the wurtzite facet (Figure 4a). In a different piece of work, the same authors showed that the epitaxial growth of ZB derived tips in rugby ball shaped polytypic $\text{Cu}_2\text{CdSn}(\text{SSe})_4$ nanocrystals can be localized to just one {002} facet of wurtzite disc by increasing the Cd molar concentration in the reaction flask to form bullet-shaped geometry.⁴ Besides the formation of this linear geometry, branched morphology is also possible in the quaternary systems. Cabot and co-workers were successful in synthesizing polarity driven branched $\text{Cu}_2\text{CdSnSe}_4$ nanocrystals.³⁹ The initial seeds are zincblende in nature with pentahedral morphology giving rise to wurtzite derived branches by a twinning mechanism (Figure 4b).

The number of interfaces shared between the two phases, that is, WZ and ZB and their size ratio, is also controllable in multinary nanocrystals. We have recently observed that by judicious selection of ligands and metal precursors, the shape of linear polytypic nanocrystals can be tuned from ellipsoids to arrow shaped to bullet shaped in $\text{Cu}_2\text{ZnSn}(\text{SSe})_4$ (CZTSSe) nanocrystals (Figure 4c–e).⁴⁰

Controlling Factors for the Occurrence and Tuning of Polytypism. Phase-selective growth to produce polytypic nanocrystals

Phase-selective growth to produce polytypic nanocrystals requires a fine balance between the different control factors involved in the reaction kinetics, specifically, the temperature, ligand chemistry, presence of additives, and choice of precursors and their reactivity.

requires a fine balance between the different control factors involved in the reaction kinetics, specifically, the temperature, ligand chemistry, presence of additives, and choice of precursors and their reactivity. The influence of each of these factors is detailed in the following section

Temperature. Temperature plays an important role in the colloidal reaction kinetics as it determines the activation energy for the nucleation and growth processes. Most of the colloidal syntheses are carried out between room temperature and 350 °C, with the upper limit dictated by the boiling point of solvent/surfactants that are used.^{41,42} This range facilitates the separate temperature zones effective for nucleation and growth of nanocrystals.⁴³ Nanocrystals can be synthesized by the hot-injection approach (most common), where nucleation occurs on rapid supersaturation or by one-pot noninjection methods with nucleation initiators.^{44,45} A rapid temperature perturbations often instigates polytypism in the growing nanocrystals.³⁶ During the formation of II–VI semiconductor branched morphologies, the germination occurs in kinetically favored ZB phase at low temperature and the rapid temperature ramp allows the formation of thermodynamically stable WZ phase.³ During the synthesis of multicomponent copper chalcogenides, we have observed that the temperature range for the growth of WZ phase is 220–280 °C and for ZB growth is 255–310 °C.³⁷ If the nucleation temperature is higher (>280 °C) than the growth temperature then the resulting nanocrystals tend to have the 3-D morphology with a tetrahedrally coordinated ZB core and WZ derived arms. Contrary to this, when the nucleation is achieved at a much lower temperature (<220 °C) with the growth at higher temperatures, 1-D linear structures are formed having a WZ core and two ZB-derived tips on either end.

Ligand Chemistry. The chemical nature and physical dimension of the ligands used in the colloidal synthesis of nanocrystals have a huge impact on the structure, morphology, and stability of the resulting nanocrystals. The understanding of the role of ligands during nucleation and growth is essential to help the system break the inversion symmetry of the crystal structure, which is an intrinsic requirement for growth of biphasic nanocrystals.⁴⁶ One of the most exploited classes of ligands in semiconductor nanocrystal growth via colloidal approach constitutes alkylphosphonic acids. This is mainly due to the following three reasons: (i) they are the strongest binding ligands among TOPO, amines and fatty acids confirmed by DFT calculations,²² (ii) the [cation–phosphonate] complexes are stable even at high temperature for hot injection colloidal methods,⁴¹ and (iii) the lengths of the alkyl chains associated with them has a strong impact on the equilibrium between the wurtzite and zincblende polytypes.⁵

Many researchers have reported the effect of alkyl chain length of a phosphonic acid over the formation mechanism during the synthesis of branched morphologies in Cd containing semiconductor nanocrystals.^{5,9} It is widely accepted that the shorter chain phosphonic ligands stimulate the anisotropic growth (WZ) in the II–VI nanocrystals.⁵ A simpler explanation is that the complex between the cationic species and the short chain ligands react more rapidly to form nuclei upon reaction with the anionic precursor. Due to lower steric hindrance, diffusion of the nuclei is faster, consequently leading to anisotropic shape evolution. The vice versa applies to the longer chain phosphonic acids. Hence, mixtures of different chain length phosphonic acids in an optimized molar ratio gives control over length and degree of branching in the synthesized nanocrystals.^{47,48}

Impurities/Additives. Interestingly, the growth kinetics of the colloidal nanocrystals can be dramatically influenced by the impurities present in the batch of chemical employed for synthesis. Manna and his co-workers found that when very pure octadecylphosphonic acid (ODPA, 99%) was used for synthesizing CdTe, spherical nanocrystals were obtained, whereas when low-purity commercially available ODPA was used, nanorods or tetrapods were formed.⁴⁸ The impurities present in the low-purity ODPA batch were the shorter chain phosphonic acids such as methyl phosphonic acid and propyl phosphonic acids, which fostered the branching in CdTe nanocrystals.

For the synthesis of multinary copper-based metal chalcogenide such as CIS, CIGS, CZTS, CZTSSe in wurtzite phase, oleylamine (OLA) and hexyldecylamine has been widely due to their dual function as coordinating solvent and ligand. We have observed during the formation of CTS, CZTS, and CZTSSe polytypic nanocrystals, that OLA clearly favors the wurtzite phase formation at low temperatures either as nucleating seed or as an extension of zincblende derived seed in the form of elongated pods.^{36–38}

Precursor Chemistry. For synthesizing monodisperse binary, ternary, or quaternary semiconductor nanocrystals, the reactivity of the ionic precursors and the ligands should be well balanced. This is best achieved by applying Pearson's hard and soft acids and bases (HSAB) principle, originally developed for metal coordination compounds, to the bonding of molecular species to the nanocrystal surface and to identify the ideal precursors for controlling the reaction rate.⁴⁹ The initial syntheses of Cd based polytypic nanocrystal were achieved with alkylcadmium precursors as they are the most reactive cadmium source.^{6,11} With the advancement of the colloidal chemistry, the highly toxic precursors were replaced by low toxic cadmium oxide (CdO) having moderate reactivity in the reaction, which could be tuned by judicious selection of ligands.⁸ The reactivity is best balanced by introduction of the anions in the form of phosphine complexes, such as trioctylphosphine (TOP)–chalcogen (TOP-Te, TOP-Se), which facilitate the formation of zincblende seeds at high temperatures and further interplay of precursors and ligands lead to growth extension in wurtzite phases.^{8,22}

For multinary metal chalcogenides, due to the involvement of four or five metal precursors in one system, the HSAB principle cannot be used to predict all possible precursor–ligand exchange routes. From detailed in situ studies on growth and nucleation of copper-based metal chalcogenide nanocrystals, it was found that Cu^+ is the most reactive species in the colloidal solution.⁵⁰ The reactivity of its precursor and the interaction with the ligand decides the rate of nucleation and number of nuclei formed during nucleation. Wang et al. discovered that the use of copper chloride (Cu(I)Cl) (highly reactive Cu source) along with tin chloride as metal precursors provided optimal control over separation of nucleation and growth events to form polytypic Cu_2SnSe_3 tetrapod and linear heterostructures.³⁷ Coughlan et al. for CZTS polytypic nanocrystals reported that the combination of metal chlorides as precursors along with OLA prompts the growth of biphasic heterostructures.³⁸ We have observed lately that by separating out the role of precursor and ligand species, it is possible to tune the shape and phases of complex polytypic structures.⁴⁰ When (Cu(I)Cl) is used as copper precursor it facilitates rapid growth on both {002} facets and the occurrence of large ZB-derived tips to form ellipsoidal shaped crystals. On the other hand, when copper acetate (Cu(I)OAc) was used as precursor,

growth of zincblende tip was localized to only one (001) facet of wurtzite disc. Both Cu(I)Cl and Cu(I)OAc are the combination of a soft acid (Cu^+) and a hard base (Cl^-/OAc^-). However, as the acetate is a softer base than the chloride (0.16 eV vs 2.49 eV, respectively), this makes Cu(I)OAc less reactive than Cu(I)Cl . As the {002} facets of wurtzite terminate in either a row of metal or chalcogen respectively, the opposite ends have different polarity and surface energies and are passivated differently by the available surfactant species. With a less reactive copper precursor, this manifests as a preference for growth at one end most likely the chalcogen terminated as the ligand species are optimized for interaction with the metal ions.

Application and Future Outlook. The wide range of control parameters and complex chemistry makes polytypes some of the most interesting and challenging structures in colloidal nanocrystal chemistry. Progression in our understanding of polytypism from a random event to a controllable phenomenon is critical to the application of semiconductor nanocrystals. In applications requiring single crystal nanostructures for example, spontaneous polytypism is undesirable as regions of different phases can act as electron traps or recombination centers.

A better understanding of polytypism would help control the occurrence when not required but, equally significantly, would allow for design of a wide range of new materials and properties that benefit from polytypic transformations.

A better understanding of polytypism would help control the occurrence when not required but, equally significantly, would allow for design of a wide range of new materials and properties that benefit from polytypic transformations. For example, polytypes are particularly interesting for thermoelectric, as the small grain sizes and variation in band structure for different phases allow independent tuning of thermal and electrical conductivity to maximize the seebeck coefficient. Arbiol, Cabot, and co-workers reported the 2.5-fold enhancement of thermoelectric figure of merit for ternary Cu_2GeSe_3 (CGSe) nanocrystals by synthesizing polytypic CGSe nanoparticles with disordered cation positions.⁵³ By carefully adjusting the nucleation and growth temperatures, a high density of twin disorders were created to periodically change the atomic plane stacking, forming a hexagonal wurtzite CGSe phase between layers of zincblende phase.

The branched shape evolution possible also leads to shape-dependent properties not attainable with single crystal structures such as tetrapod photovoltaics,⁵⁴ where the branches act as antennae for light harvesting, or as single electron transistors,⁵⁵ where the core acts as a quantum well, with the pods providing contacting and gating functionality.

In more complex quaternary polytypes, the lack of cation ordering in the branches shrinks the band gap energy and shifts the Fermi energy into the conduction band giving the branches a metallic character that are interesting for surface plasmonic devices.⁵⁶ Organisation of polytypes into superstructures is also interesting (Figure 5a–d).^{51,57} Manna and co-workers showed that hierarchical organization of octapods could be achieved by

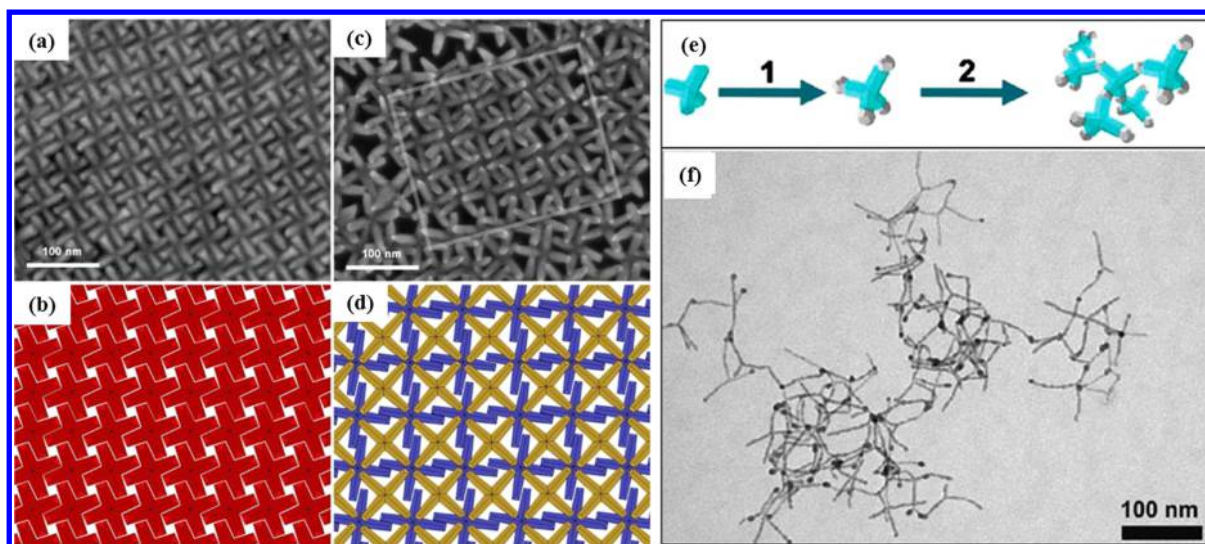


Figure 5. (a–d) Assembly of octapods on a flat substrate following solvent evaporation. (e) Schematic of self-assembly of tetrapods by the nanowelding approach. (f) TEM image of nanowelding assembly. Reproduced with permission from ref 51 and 52. Copyright 2012, American Chemical Society, and Copyright 2009, John Wiley & Sons.

slowly decreasing the stability of the octapods in solution.⁵⁸ Later self-assembly by “nanowelding” approach was also introduced by same authors to allow better electron transport.⁵² They showed that coalescence of gold domains tipped at the ends of the branches of tetrapods lead to the formation of disordered 3-D superstructures welded together through gold particles (Figure 5e,f).

Ultimately, controlled polytypic transformations in nanocrystals offer exciting opportunities for materials design, where complex branched nanostructures can be defined across a range of material compositions, assembled into superstructures, and demonstrate heretofore unachievable material properties defined by their polytypic construct.

AUTHOR INFORMATION

Corresponding Author

*E-mail: Kevin.M.Ryan@ul.ie.

Notes

The authors declare no competing financial interest.

Biographies

Shalini Singh is currently a Ph.D. candidate in Chemistry at University of Limerick, Ireland, under the supervision of Dr. Kevin M. Ryan. She earned M.Sc. from D.D.U. Gorakhpur University, India. Her research is focused on the development of shape, phase, and compositionally tunable colloidal semiconductor nanocrystals for energy conversion applications.

Kevin M. Ryan is currently Senior Lecturer in Chemical Nanotechnology at the University of Limerick, Ireland. His group’s research interests are in nanostructure synthesis, assembly, and applications in energy storage and energy conversion. He previously held Marie Curie Fellowship positions at the UC Berkeley, and Merck Chemicals U.K., following B.Sc. and Ph.D. degrees from University College Cork.

ACKNOWLEDGMENTS

This work was supported principally by Science Foundation Ireland (SFI) under the Principal Investigator Program (Contract No. 11PI-1148) and was conducted under the framework of the Irish Government’s Programme for Research in Third Level Institutions Cycle 5, National Development Plan 2007–2013

with the assistance of the European Regional Development Fund.

REFERENCES

- (1) Park, C. H.; Cheong, B.-H.; Lee, K.-H.; Chang, K. J. Structural and electronic properties of cubic, 2H, 4H, and 6H SiC. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *49*, 4485–4493.
- (2) Yeh, C.-Y.; Lu, Z. W.; Froyen, S.; Zunger, A. Zincblende-wurtzite polytypism in semiconductors. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *46*, 10086–10097.
- (3) Deka, S.; Misztal, K.; Dorfs, D.; Genovese, A.; Bertoni, G.; Manna, L. Octapod-shaped colloidal nanocrystals of cadmium chalcogenides via “one-pot” cation exchange and seeded growth. *Nano Lett.* **2010**, *10*, 3770–3776.
- (4) Wu, L.; Fan, F. J.; Gong, M.; Ge, J.; Yu, S. H. Selective epitaxial growth of zincblende-derivative on wurtzite-derivative: the case of polytypic $\text{Cu}_2\text{CdSn}(\text{S}_{(1-x)}\text{Se}_x)_4$ nanocrystals. *Nanoscale* **2014**, *6*, 3418–3422.
- (5) Huang, J.; Kovalenko, M. V.; Talapin, D. V. Alkyl chains of surface ligands affect polytypism of CdSe nanocrystals and play an important role in the synthesis of anisotropic nanoheterostructures. *J. Am. Chem. Soc.* **2010**, *132*, 15866–15868.
- (6) Manna, L.; Scher, E. C.; Alivisatos, A. P. Synthesis of soluble and processable rod-, arrow-, teardrop-, and tetrapod-shaped CdSe nanocrystals. *J. Am. Chem. Soc.* **2000**, *122*, 12700–12706.
- (7) Kanaras, A. G.; Sönnichsen, C.; Liu, H.; Alivisatos, A. P. Controlled synthesis of hyperbranched inorganic nanocrystals with rich three-dimensional structures. *Nano Lett.* **2005**, *5*, 2164–2167.
- (8) Manna, L.; Milliron, D. J.; Meisel, A.; Scher, E. C.; Alivisatos, A. P. Controlled growth of tetrapod-branched inorganic nanocrystals. *Nat. Mater.* **2003**, *2*, 382–385.
- (9) Yu, W. W.; Wang, Y. A.; Peng, X. Formation and stability of size-, shape-, and structure-controlled CdTe nanocrystals: ligand effects on monomers and nanocrystals. *Chem. Mater.* **2003**, *15*, 4300–4308.
- (10) Chen, M.; Xie, Y.; Lu, J.; Xiong, Y.; Zhang, S.; Qian, Y.; Liu, X. Synthesis of rod-, twinrod-, and tetrapod-shaped CdS nanocrystals using a highly oriented solvothermal recrystallization technique. *J. Mater. Chem.* **2002**, *12*, 748–753.
- (11) Jun, Y.-w.; Lee, S.-M.; Kang, N.-J.; Cheon, J. Controlled synthesis of multi-armed CdS nanorod architectures using mono-surfactant system. *J. Am. Chem. Soc.* **2001**, *123*, 5150–5151.
- (12) Xi, B.; Xu, D.; Xiong, S.; Wang, C.; Feng, X.; Zhou, H.; Qian, Y. Preparation and characterization of cubic and hexagonal polytypes of

ZnSe:Cu²⁺ one-dimensional nanostructures. *J. Phys. Chem. C* **2008**, *112*, 5333–5338.

(13) Cozzoli, P. D.; Manna, L.; Curri, M. L.; Kudera, S.; Giannini, C.; Striccoli, M.; Agostiano, A. Shape and phase control of colloidal ZnSe nanocrystals. *Chem. Mater.* **2005**, *17*, 1296–1306.

(14) Jiang, F.; Li, Y.; Ye, M.; Fan, L.; Ding, Y.; Li, Y. Ligand-tuned shape control, oriented assembly, and electrochemical characterization of colloidal ZnTe nanocrystals. *Chem. Mater.* **2010**, *22*, 4632–4641.

(15) Brescia, R.; Misztal, K.; Dorfs, D.; Manna, L.; Berton, G. Birth and growth of octapod-shaped colloidal nanocrystals studied by electron tomography. *J. Phys. Chem. C* **2011**, *115*, 20128–20133.

(16) Fan, F.-J.; Wu, L.; Gong, M.; Chen, S. Y.; Liu, G. Y.; Yao, H.-B.; Liang, H.-W.; Wang, Y.-X.; Yu, S.-H. Linearly arranged polytypic CZTSSe nanocrystals. *Sci. Rep.* **2012**, *2*, 952.

(17) Kuno, M.; Ahmad, O.; Protasenko, V.; Bacinello, D.; Kosel, T. H. Solution-based straight and branched CdTe nanowires. *Chem. Mater.* **2006**, *18*, 5722–5732.

(18) Hughes, S. M.; Alivisatos, A. P. Anisotropic formation and distribution of stacking faults in II–VI semiconductor nanorods. *Nano Lett.* **2013**, *13*, 106–110.

(19) Yao, Y.; Kuroda, T.; Dirin, D. N.; Irkhina, A. A.; Vasiliev, R. B.; Sakoda, K. Exciton states of II–VI tetrapod-shaped nanocrystals. *Opt. Mater. Express* **2013**, *3*, 977–988.

(20) Mahler, B.; Lequeux, N.; Dubertret, B. Ligand-controlled polytypism of thick-shell CdSe/CdS nanocrystals. *J. Am. Chem. Soc.* **2010**, *132*, 953–959.

(21) Fan, Z.; Yalcin, A. O.; Tichelaar, F. D.; Zandbergen, H. W.; Talgorn, E.; Houtepen, A. J.; Vlucht, T. J.; van Huis, M. A. From sphere to multipod: thermally induced transitions of CdSe nanocrystals studied by molecular dynamics simulations. *J. Am. Chem. Soc.* **2013**, *135*, 5869–5876.

(22) Asokan, S.; Krueger, K. M.; Colvin, V. L.; Wong, M. S. Shape-controlled synthesis of CdSe tetrapods using cationic surfactant ligands. *Small* **2007**, *3*, 1164–1169.

(23) Gao, Y.; Peng, X. Crystal structure control of CdSe nanocrystals in growth and nucleation: dominating effects of surface versus interior structure. *J. Am. Chem. Soc.* **2014**, *136*, 6724–32.

(24) Kim, M. R.; Misztal, K.; Povia, M.; Brescia, R.; Christodoulou, S.; Prato, M.; Marras, S.; Manna, L. Influence of chloride ions on the synthesis of colloidal branched CdSe/CdS nanocrystals by seeded growth. *ACS Nano* **2012**, *6*, 11088–11096.

(25) Fanfair, D. D.; Korgel, B. A. Twin-related branching of solution-grown ZnSe nanowires. *Chem. Mater.* **2007**, *19*, 4943–4948.

(26) Wang, J.; Yang, Q. One-dimensional angle-shaped ZnSe nanostructures: synthesis and formation mechanism. *Cryst. Growth Des.* **2008**, *8*, 660–664.

(27) Aldakov, D.; Lefrançois, A.; Reiss, P. Ternary and quaternary metal chalcogenide nanocrystals: synthesis, properties and applications. *J. Mater. Chem. C* **2013**, *1*, 3756–3776.

(28) Singh, A.; Coughlan, C.; Laffir, F.; Ryan, K. M. Assembly of CuIn_{1-x}Ga_xS₂ nanorods into highly ordered 2D and 3D superstructures. *ACS Nano* **2012**, *6*, 6977–6983.

(29) Koo, B.; Patel, R. N.; Korgel, B. A. Wurtzite–chalcopyrite polytypism in CuInS₂ nanodisks. *Chem. Mater.* **2009**, *21*, 1962–1966.

(30) Yin, Z.; Hu, Z.; Ye, H.; Teng, F.; Yang, C.; Tang, A. One-pot controllable synthesis of wurtzite CuInS₂ nanoplates. *Appl. Surf. Sci.* **2014**, *307*, 489–494.

(31) Liu, Z.; Wang, L.; Hao, Q.; Wang, D.; Tang, K.; Zuo, M.; Yang, Q. Facile synthesis and characterization of CuInS₂ nanocrystals with different structures and shapes. *CrystEngComm* **2013**, *15*, 7192–7198.

(32) Vahidshad, Y.; Nawaz Tahir, M.; Iraj Zad, A.; Mirkazemi, S. M.; Ghasemzadeh, R.; Huesmann, H.; Tremel, W. Structural and optical study of Ga³⁺ substitution in CuInS₂ nanoparticles synthesized by a one-pot facile method. *J. Phys. Chem. C* **2014**, *118*, 24670–24679.

(33) Connor, S. T.; Weil, B. D.; Misra, S.; Cui, Y.; Toney, M. F. Behaviors of Fe, Zn, and Ga substitution in CuInS₂ nanoparticles probed with anomalous X-ray diffraction. *Chem. Mater.* **2013**, *25*, 320–325.

(34) Liu, Z.; Hao, Q.; Tang, R.; Wang, L.; Tang, K. Facile one-pot synthesis of polytypic CuGaS₂ nanoplates. *Nanoscale Res. Lett.* **2013**, *8*, 1–6.

(35) Kluge, O.; Friedrich, D.; Wagner, G.; Krautscheid, H. New organometallic single-source precursors for CuGaS₂-polytypism in gallite nanocrystals obtained by thermolysis. *Dalton Trans.* **2012**, *41*, 8635–8642.

(36) Wang, J.; Singh, A.; Liu, P.; Singh, S.; Coughlan, C.; Guo, Y.; Ryan, K. M. Colloidal synthesis of Cu₂SnSe₃ tetrapod nanocrystals. *J. Am. Chem. Soc.* **2013**, *135*, 7835–7838.

(37) Wang, J.-j.; Liu, P.; Seaton, C. C.; Ryan, K. M. Complete colloidal synthesis of Cu₂SnSe₃ nanocrystals with crystal phase and shape control. *J. Am. Chem. Soc.* **2014**, *136*, 7954–7960.

(38) Coughlan, C.; Ryan, K. M. Complete study of the composition and shape evolution in the synthesis of Cu₂ZnSnS₄ (CZTS) semiconductor nanocrystals. *CrystEngComm* **2015**, DOI: 10.1039/C5CE00497G.

(39) Zamani, R. R.; Ibáñez, M.; Luysberg, M.; García-Castelló, N.; Houben, L.; Prades, J. D.; Grillo, V.; Dunin-Borkowski, R. E.; Morante, J. R.; Cabot, A.; Arbiol, J. Polarity-driven polytypic branching in Cu-based quaternary chalcogenide nanostructures. *ACS Nano* **2014**, *8*, 2290–2301.

(40) Singh, S.; Liu, P.; Singh, A.; Coughlan, C.; Wang, J.; Lusi, M.; Ryan, K. M. Colloidal Cu₂ZnSn(SSe)₄ (CZTSSe) nanocrystals: shape and crystal phase control to form dots, arrows, ellipsoids, and rods. *Chem. Mater.* **2015**, *27*, 4742–4748.

(41) Singh, S.; Singh, A.; Palaniappan, K.; Ryan, K. M. Colloidal synthesis of homogeneously alloyed CdSe_xS_{1-x} nanorods with compositionally tunable photoluminescence. *Chem. Commun.* **2013**, *49*, 10293–10295.

(42) Singh, A.; Singh, S.; Levchenko, S.; Unold, T.; Laffir, F.; Ryan, K. M. Compositionally tunable photoluminescence emission in Cu₂ZnSn(S_{1-x}Se_x)₄ nanocrystals. *Angew. Chem., Int. Ed.* **2013**, *52*, 9120–9124.

(43) Pradhan, N.; Reifsnnyder, D.; Xie, R.; Aldana, J.; Peng, X. Surface ligand dynamics in growth of nanocrystals. *J. Am. Chem. Soc.* **2007**, *129*, 9500–9509.

(44) Cao, Y. C.; Wang, J. One-pot synthesis of high-quality zincblende CdS nanocrystals. *J. Am. Chem. Soc.* **2004**, *126*, 14336–14337.

(45) Yang, Y. A.; Wu, H.; Williams, K. R.; Cao, Y. C. Synthesis of CdSe and CdTe nanocrystals without precursor injection. *Angew. Chem., Int. Ed.* **2005**, *44*, 6712–6715.

(46) Nag, A.; Hazarika, A.; Shanavas, K. V.; Sharma, S. M.; Dasgupta, I.; Sarma, D. D. Crystal structure engineering by fine-tuning the surface energy: the case of CdE (E = S/Se) nanocrystals. *J. Phys. Chem. Lett.* **2011**, *2*, 706–712.

(47) Wang, W.; Banerjee, S.; Jia, S.; Steigerwald, M. L.; Herman, I. P. Ligand control of growth, morphology, and capping structure of colloidal CdSe nanorods. *Chem. Mater.* **2007**, *19*, 2573–2580.

(48) Carbone, L.; Kudera, S.; Carlino, E.; Parak, W. J.; Giannini, C.; Cingolani, R.; Manna, L. Multiple wurtzite twinning in CdTe nanocrystals induced by methylphosphonic acid. *J. Am. Chem. Soc.* **2006**, *128*, 748–755.

(49) Pearson, R. G. Hard and soft acids and bases. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.

(50) Tan, J. M.; Lee, Y. H.; Pedireddy, S.; Baikia, T.; Ling, X. Y.; Wong, L. H. Understanding the synthetic pathway of a single-phase quaternary semiconductor using surface-enhanced Raman scattering: a case of wurtzite Cu₂ZnSnS₄ nanoparticles. *J. Am. Chem. Soc.* **2014**, *136*, 6684–92.

(51) Qi, W.; Graaf, J. d.; Qiao, F.; Marras, S.; Manna, L.; Dijkstra, M. Ordered two-dimensional superstructures of colloidal octapod-shaped nanocrystals on flat substrates. *Nano Lett.* **2012**, *12*, 5299–5303.

(52) Figuerola, A.; Franchini, I. R.; Fiore, A.; Mastria, R.; Falqui, A.; Berton, G.; Bals, S.; Van Tendeloo, G.; Kudera, S.; Cingolani, R.; Manna, L. End-to-end assembly of shape-controlled nanocrystals via a nanowelding approach mediated by gold domains. *Adv. Mater.* **2009**, *21*, 550–554.

(53) Ibáñez, M.; Zamani, R.; Li, W.; Cadavid, D.; Gorsse, S.; Katcho, N. A.; Shavel, A.; López, A. M.; Morante, J. R.; Arbiol, J.; Cabot, A. Crystallographic control at the nanoscale to enhance functionality: polytypic Cu_2GeSe_3 nanoparticles as thermoelectric materials. *Chem. Mater.* **2012**, *24*, 4615–4622.

(54) Sun, B.; Marx, E.; Greenham, N. C. Photovoltaic devices using blends of branched CdSe nanoparticles and conjugated polymers. *Nano Lett.* **2003**, *3*, 961–963.

(55) Cui, Y.; Banin, U.; Björk, M. T.; Alivisatos, A. P. Electrical transport through a single nanoscale semiconductor branch point. *Nano Lett.* **2005**, *5*, 1519–1523.

(56) Orendorff, C. J.; Gole, A.; Sau, T. K.; Murphy, C. J. Surface-enhanced raman spectroscopy of self-assembled monolayers: sandwich architecture and nanoparticle shape dependence. *Anal. Chem.* **2005**, *77*, 3261–3266.

(57) Zanella, M.; Bertoni, G.; Franchini, I. R.; Brescia, R.; Baranov, D.; Manna, L. Assembly of shape-controlled nanocrystals by depletion attraction. *Chem. Commun.* **2011**, *47*, 203–205.

(58) Miszta, K.; de Graaf, J.; Bertoni, G.; Dorfs, D.; Brescia, R.; Marras, S.; Ceseracciu, L.; Cingolani, R.; van Roij, R.; Dijkstra, M.; Manna, L. Hierarchical self-assembly of suspended branched colloidal nanocrystals into superlattice structures. *Nat. Mater.* **2011**, *10*, 872–876.