Emerging strategies for the synthesis of highly monodisperse colloidal nanostructures

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This short perspective describes recent developments in the synthesis of nanoscale colloids from sparingly soluble precursors. These strategies, which we dubbed ‘heterogeneous nanocrystal syntheses’ owing to the presence of a precursor in a non-colloidal solid state, have demonstrated the ability to generate new colloidal shapes, a superior monodispersity and a remarkable ability to delay the onset of Ostwald ripening, when compared with more traditional and purely colloidal strategies. We review the key contributions to this emerging area of research and discuss in detail the remarkable number of differences between these syntheses and the widely used homogeneous organometallic syntheses for making nanoscale colloids.

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1. Introduction

Nanotechnology is, in part, a new way of thinking about materials and how to use them to solve problems. From this perspective, it is clearer how nanotechnology has its roots into materials chemistry (Whitesides et al. 1991; Ozin 1992; Weller 1993; Gleiter 2000; Niemeyer 2001; Colfen & Mann 2003; Oberdorster et al. 2005; Descalzo et al. 2006; Feldkamp & Niemeyer 2006; Henzie et al. 2006; Ariga et al. 2007; Billinge & Levin 2007; Darling 2007; Long et al. 2007; Balzani et al. 2008; Palmer & Stupp 2008). The relation between the two is defined by nanoochemistry (Cademartiri & Ozin 2009a,b; Ozin & Cademartiri 2009; Ozin et al. 2009), a branch of chemistry devoted to the synthesis, characterization and assembly of nanoscale chemical constructs—the building blocks of bottom-up nanotechnology.

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In the past 20–30 years, the major developments in nanotechnology have been mostly heralded by breakthroughs in either the synthesis of well-defined nanostructures (as for colloidal quantum dots; Murray et al. 1993) or the development of analytical techniques for their characterization (as for scanning probe microscopy; Binnig & Rohrer 1986; Binnig et al. 1986).

From a chemistry perspective, the synthesis of well-defined building blocks for bottom-up nanotechnology is a fascinating and ever-stimulating challenge. The key targets for the chemistry of nanostructures can be summarized as follows:

— the formulation of a general strategy for the synthesis of perfectly (atomically) monodisperse nanostructures, with and without a ligand shell;
— the development of syntheses that can be scaled to industrial scale in green conditions, while retaining the perfection obtainable in a research laboratory setting;
— the development of a general strategy for the formation of hybrid (multi-component) nanostructures with perfectly defined shapes, crystal boundaries and properties;
— the development of a general strategy for the design of surface chemistry on specific locations of the nanostructure to enable spatially directed interactions among nanocrystals;
— the understanding of the physico-chemical consequences, atom-by-atom, of size, shape, surface structure, composition and defects.

While it is evident that important strides have been made in the abovementioned directions, we feel that their achievement is not yet in sight (Ozin & Cademartiri 2009).

We would like to especially emphasize how universality and perfection, in terms of structure and monodispersity, is not just an academic exercise for the aesthetically minded, but in most cases a prerequisite for a conclusive physico-chemical understanding of structure–property–function relationships and how these pertain to utility. Much of the difficulty in modern nanochemistry research lies in having to deal with large amounts of literature where physico-chemical conclusions are drawn from samples that are widely different, and sometimes questionable and difficult to reproduce, in their level of homogeneity and perfection.

The pursuit of the abovementioned objectives is worth considering not only because of the science behind them, but also because they would, in our opinion, be the only way to fulfil the true potential of nanomatter engineered at the atomic scale. The fundamental step for chemistry to become a societally useful science was when molecules of completely determined structure and fundamental properties could be produced in gigatonne quantities, with nearly arbitrary purity, and at prices that would be competitive with the extraction of the competing natural products. Nanochemistry is by any standards not there yet.

It is in this framework that the subject of this short perspective is centred. If we take the field of quantum dots as representative—and we do believe it to be one of the best success stories of nanochemistry—while the syntheses developed in the late 1980s and early 1990s were efficient and led to an explosion of interest and literature, they were lacking in many respects. Those syntheses were generally non-scalable, difficult, often requiring relatively high
temperatures, as well as dangerous and often costly reagents (Steigerwald et al. 1988; Steigerwald & Brus 1989; Murray et al. 1993; Hines & Guyot-Sionnest 1996; Dabbousi et al. 1997; Peng et al. 1997). Similar considerations can be made for other nanostructures beside quantum dots. The investigations by Peng’s group at the beginning of this century of alternative routes to nanocrystal syntheses amplified the access to these materials by using safer chemicals and slightly lower temperatures (Qu et al. 2001; Peng & Peng 2002; Li et al. 2003).

We believe that we might be at the emergence of a new strategy for the synthesis of nanostructures, which will simultaneously simplify and improve the preparation of nanostructures, by using relatively safe reagents, at relatively low temperatures, yielding structures of better quality—a soft(er) nanochemistry. These new syntheses allow for (i) the production of multi-gram quantities of nanostructures in a single laboratory-scale reaction, (ii) the recycling of unused precursors, (iii) the use of far higher concentrations (which reduces the consumption of solvents), and (iv) a remarkably different growth kinetic with unexpected consequences on the product’s morphology and size. This strategy is based on the use of heterogeneous reaction environments, and it is the subject of this short perspective.

Colloidal nanostructures are, in large part, synthesized in organic solvents, where organometallic precursors are reacted at high temperatures in the presence of amphiphilic molecules, which act as capping ligands on the surface of the nanostructured product. The nucleation is generally induced by a fast injection of one or both precursors into the hot reaction vessel (Murray et al. 1993; Donega et al. 2005) or by decomposing the precursor at a certain temperature (Kwon et al. 2007). Both approaches have been demonstrated to be analogous in terms of separating nucleation and growth. LaMer & Dinegar (1950) showed in the 1950s how the separation of the nucleation and growth process would be fundamental to the achievement of narrowly dispersed colloids. Their model is still the cardinal working framework for most monodisperse colloidal syntheses.

In the case of hot injection techniques, the nucleation is arrested by the sudden decrease in temperature following the injection. This is thought to halt nucleation and to prevent it from consuming most of the available precursors, which would lead to a fast aggregation and ripening process. Upon reaching an appropriate temperature (generally lower than the temperature of injection, but higher than the minimal temperature reached after the injection), the previously formed nuclei grow all at the same time. The large supersaturation left after injection leads to a uniform growth of all nuclei at very similar rates, thus decreasing the size dispersion. This phase is called focusing, it has been shown in countless examples of organometallic nanocrystals syntheses and it is widely regarded as the main reason for the remarkable success of hot injection (or decomposition) techniques in obtaining colloidal products with low polydispersity (approx. 4–6%) (Peng et al. 1998).

The growth of the particles happens at the expense of the supersaturation. According to the standard Gibbs picture, this decrease in the available precursor concentration implies an increase in the critical radius. The critical radius determines the size below which particles are more likely to dissolve, and above which particles are more likely to grow, and it is expressed as \( r^* = \frac{2 \Omega \gamma}{k_B T \ln(S)} \), where \( S \) is the supersaturation, \( \gamma \) is the free energy required to generate a unit area of surface interface and \( \Omega \) is the volume occupied by a
formula unit in the particle nucleus (Carter 1996). Some big assumptions behind this picture are that the nucleus is spherical and that surface energies can be well defined for such small nanocrystals.

As the monomers are consumed during the growth of the particles, the supersaturation decreases, leading to an increase in the critical radius. This can reach the point where $r^*$ becomes larger than the radius of a fraction of the particles in solution. This means that those particles will start dissolving, while the particle fraction whose radius is larger than $r^*$ will grow at their expense. This phenomenon, called Ostwald ripening (defocusing), is responsible for most of the size broadening of nanocrystals in solutions at low supersaturation (or long growth time).

Ostwald ripening leads to an equilibrium polydispersity of approximately 20 per cent (Talapin et al. 2001), which is far broader than what is attainable by quenching the reaction before ripening occurs. Polydispersities of 4–6% are now customary for optimized reaction protocols. It is then clear how limiting Ostwald ripening is a key target for any nanocrystal chemist. The problem of how to do it is fairly complex as it entails a compromise between various aspects of the precursors.

In general, it is preferable to have fairly stable precursors. This allows for a better control over the growth of the particles, besides being generally safer, greener and cheaper (Peng 2002). Highly reactive precursors generate too many nuclei and thus deplete too soon after injection, leading to an early onset of ripening. Precursors that are not reactive enough will not generate many nuclei and will lead to large particles—the onset of ripening will be delayed but the particles might be already too big to be useful.

There are several strategies that have been used to avoid Ostwald ripening. In several cases, the supersaturation is replenished by adding more precursors during the growth. This can cause several problems as the addition can lead to secondary nucleation or dendritic growth (Milliron et al. 2004).

Another approach has made use of saturated solutions of sparingly soluble precursors to ensure the constant delivery of molecular precursors to the reaction (Cadernartiri et al. 2005; Evanoff & Chumanov 2005; Yang et al. 2005; Park et al. 2006). These reactions are dubbed ‘heterogeneous nanocrystal syntheses’ owing to the heterogeneity of the reaction environment in which they occur. These reactions can follow an injection protocol (Cadernartiri et al. 2005) or be conducted as a one-pot synthesis (Evanoff & Chumanov 2005; Yang et al. 2005). They can produce metal nanocrystals via the gradual dissolution and reduction of a solid precursor (Evanoff & Chumanov 2005; Wang et al. 2005), or produce semiconductor nanocrystals via gradual reaction of two precursors, one of which is solid. The solid precursor is gradually consumed during the reaction: whatever has not reacted is left as a solid, which can be easily separated and reused. It is widely assumed, though not proved yet, that the solid precursor has some limited solubility and that the ‘solubilized’ molecular (or nanoscale) fraction is the one involved in the nucleation and growth of nanostructures. While thinking of solubility, one should consider that these reactions occur in strongly coordinating organic mixtures. In many cases, the ligand is the solvent. The solid is considered as a reservoir of precursor that should maintain the concentration of the solubilized (‘available’) precursor constant throughout the reaction. We believe that the interplay between the dissolution of the solid precursor and the
reaction of the available precursor is more sophisticated than this, especially if one considers the non-equilibrium conditions in which these reactions are performed, and the presence of a strongly coordinating ligand–solvent environment. The structure and reactivity of these intermediate precursors are not known, and this complicates the predictability of these routes but also make their research more appealing.

An interesting aspect of these reactions is that they enable the use of an extremely wide spectrum of precursors that were not initially considered suitable for nanocrystal synthesis because of their insolubility. The actual precursor is generated \textit{in situ} in a self-sustained fashion. This potentially allows the use as precursors of chemical structures and moieties that would not be accessible otherwise because of the difficulties in isolating and stabilizing them. In some cases, there is the possibility that the available precursor is neither a solid nor a molecule, but a nanoscale colloid or cluster that could then react with the other precursor by ion exchange (Son \textit{et al.} 2004), and thus behave as a template.

The heterogeneous nanocrystal syntheses reported so far have mostly focused on semiconductor materials and are distinguished by the use of solid precursors for either the anion or the cation.

### 2. Solid anionic precursors

The deliberate use of an insoluble anionic precursor in a heterogeneous reaction scheme was first reported, to the best of our knowledge, in 2005 by Cao’s group (Yang \textit{et al.} 2005). In that work, the authors reported the first strategy for the preparation of hydrophobic high-quality CdSe nanocrystal quantum dots by a one-pot synthesis. Their strategy relied on the controlled decomposition of cadmium myristate in octadecene (ODE) in the presence of selenium at temperatures above 200°C. Nucleation occurred while selenium was still in solid form. Selenium powder is only slightly soluble at 200°C in ODE. At 240°C, which was the reported growth temperature, selenium is a liquid, and so it could be considered dispersed but not efficiently solvated.

Figure 1 shows the evolution of the optical properties of the CdSe product during growth. As the size of the nanoparticles increases, their optical properties are changed by quantum confinement effects. By considering the calibration curves that relate optical properties of spherical CdSe nanocrystals with their size and concentration, it is possible to follow the kinetics of this reaction by monitoring the absorbance or photoluminescence of the reaction mixture. Figure 1a shows the progression of the photoluminescence peak of the sample during growth. Figure 1b shows instead the corresponding UV-VIS absorbance spectrum. Figure 1c–e shows, respectively, the diameter of the particles, their concentration and the full-width-at-half-maximum (FWHM) of their photoluminescence at several stages of the reaction. The FWHM of the characteristic absorbance or emission peaks of nanocrystal quantum dots can be considered a semiqualitative measure of their polydispersity since the FWHM from a single particle is small compared with those measured for ensembles—inhomogeneous line broadening from a distribution of particle sizes.
Figure 1. Optical and kinetic studies on the heterogeneous one-pot reaction for the synthesis of CdSe nanocrystal quantum dots. (a) Evolution of the photoluminescence spectrum as a function of the time of growth; (b) evolution of the absorbance spectrum as a function of the time of growth; (c) evolution of the average nanocrystal size with the time of growth; (d) evolution of the nanocrystal concentration with the time of growth; and (e) evolution of the photoluminescence FWHM with the time of growth. Adapted from Yang et al. (2005).

The photoluminescence and absorbance spectra show the high quality of these samples: the emission peaks are narrow and approximately Gaussian, while the absorbance spectra show several peaks corresponding to various excitonic transitions. In the nucleation stage (indicated as \( t < 0 \) in the inset of figure 1d), the number of particles increases only to rapidly and monotonically decrease soon after. This is consistent with the presence of a coalescence mechanism between particles, which has been recently demonstrated for metallic nanocrystals by in situ TEM (Zheng et al. 2009).

The ever-decreasing FWHM of the photoluminescence though indicates how the particles do not seem to suffer from Ostwald ripening even at the end of the reaction. Interestingly, this approach leads to the formation of CdSe in the zinc-blend phase, instead of the widely more common wurtzite.

One year later, Son’s group used a similar strategy for the synthesis of InSe nanostructures (figure 2; Park et al. 2006). They reacted InCl\(_3\) and selenium powder using oleylamine as the solvent and ligand in a one-pot fashion. The
temperature was increased from the initial 110°C to 210°C, where it was kept for 5 h. In this case, the authors made an interesting comparison between two reaction strategies. In one case, they did not dissolve the selenium beforehand, thus leading the reaction to start in the presence of solid selenium. In the other case, they dissolved the selenium before initiating the reaction.

In the first heterogeneous case, they obtained wires of remarkably small thickness polydispersity. Their diameter could be tuned by varying the precursor ratio—more Se made thinner and longer wires. In this way, they were able to obtain wires approaching the ultrathin regime ($d = 2.5\,\text{nm}$).

Ultrathin nanoplates (260 nm in width by 1.8 nm in thickness) were instead obtained when selenium was used in a dissolved state.

The interesting aspect of this reaction is that by changing the state of the anionic precursor, from solid to dissolved, and thus changing the reaction from heterogeneous to homogeneous, it was possible to change not only the morphology of the product but also the symmetry of the lattice structure. The wires grew in the cubic phase of InSe, while the plates were in the hexagonal phase. The authors postulated that the two forms evolved from different growth processes: the nanowires via oriented attachment while the nanoplates via addition of monomers to highly reactive facets.

In a more recent development, Cao’s group revisited their earlier strategy by substituting Se with Se$_2$O powder (Chen et al. 2008). This modification, while small, leads to a major change in the chemistry of the reaction. The authors discovered that Se$_2$O was reduced in situ by ODE at the reaction temperatures...
to elemental Se, which then acted as a precursor for the formation of the nanocrystals. The reaction was found to be resistant to the presence of oxygen that was consumed in the early stages of the reaction, thus only delaying the onset of nucleation. This strategy was further shown to work for the synthesis of Pd$_{4.5}$Se and PbSe nanocrystals, as shown in figure 3.

3. Solid cationic precursors

The use of insoluble cationic precursors was explicitly reported in 2005 by (i) Li’s group, who reported the synthesis of a large variety of nanocrystals by a phase-transfer protocol (Wang et al. 2005), and (ii) our group with the formation of PbS nanocrystal quantum dots from the reaction of a PbCl$_2$ slurry in oleylamine.

Figure 3. Pd$_{4.5}$Se and PbSe nanostructures generated from Se$_2$O as a solid precursor. (a,b) TEM and HRTEM micrographs of PbSe nanocubes; (c) TEM micrograph of Pd$_{4.5}$Se nanocrystals; and (d) XRD of Pd$_{4.5}$Se nanocrystals. Adapted from Chen et al. (2008). Scale bars, (a) 50 nm, (b) 5 nm and (c) 20 nm.
with sulphur (Cademartiri et al. 2005). In the work of Li’s group, a phase-transfer protocol was adopted to synthesize hydrophobic nanocrystals in a polar environment (figure 4). A triphasic system was prepared by combining a solution of a metal salt, a sodium linoleate solid and a solution of linoleic acid in ethanol. The metal salt exchanged with the sodium in the solid phase, leading to a solid metal linoleate precursor that was then reduced, dehydrated or reacted at higher temperatures to generate a variety of noble metal, oxide or chalcogenide nanoparticles. In our report, a slurry of excess PbCl$_2$ in oleylamine was reacted with sulphur dissolved in oleylamine by a hot injection method, with temperatures of injection and growth being, respectively, 120°C and 100°C. The use of PbCl$_2$ in oleylamine as a precursor was reported 2 years earlier by Joo et al. (2003), but, in their experimental conditions, the powder dissolved, leading to a homogeneous solution.

In 2006 we reported an optimized heterogeneous reaction protocol based on the use of much higher concentrations of precursors (Cademartiri et al. 2006a). This improved substantially the monodispersity of the material. This reaction was later reproduced by other groups (Moreels et al. 2009; Zhao et al. 2009).
Figure 5 shows an optical analysis of the growth kinetics, depending on the reaction conditions (Cademartiri et al. 2006a). Figure 5a, b shows, respectively, the evolution of (i) the FWHM and (ii) the wavelength of the luminescence during growth for two different conditions: the filled symbols indicate low-concentration and low precursor ratio conditions that are usually found in most nanocrystal syntheses; the open symbols instead indicate a high concentration and a high precursor ratio regime, where the molarity of the ‘solvent’ and of the precursors are comparable.

The difference between the two sets of conditions is remarkable. In low-concentration conditions, the FWHM and hence the polydispersity of the nanocrystals remains essentially constant at approximately 100 meV throughout the reaction. In energy units, this peak breadth is comparable to or better than most values found in the literature for PbS quantum dots. Despite the average quality of the particles, it is worth noticing that, even after 500 min of growth, the polydispersity is not increasing as it would be expected from Ostwald ripening.

In high-concentration conditions, the results are remarkably different. The FWHM exponentially decreases for the first 20 min of the reaction, decreasing from a value of 120 meV, obtained a few seconds after the injection, to a value of 60 meV. This low polydispersity is then maintained for the remainder of the reaction.

These values of emission breadth are the lowest ever reported for PbS nanocrystal quantum dots, and among the lowest for any colloidal quantum dot, and testify to the level of monodispersity achievable with heterogeneous growth techniques.

In figure 5b, we see how the two conditions differ remarkably also in terms of the growth kinetics. Low-concentration conditions lead to a slow and steady increase in the wavelength of the emission peak from approximately 1500 to 1700 nm. Longer emission wavelengths correspond to larger sizes, owing to quantum confinement effects. At high concentrations, instead, the first 20 min
of the reaction are characterized by a fast increase in the emission wavelength (and thus of sizes), from 1250 to 1550 nm, which then slows down at a similar pace to that obtained from low-concentration conditions.

All these results can be rationalized by considering the heterogeneous nature of the reaction environment. At low concentrations of precursors, dispersed solid PbCl$_2$ and soluble S, the supersaturation at injection is relatively low, resulting in a small number of nuclei being produced. This leads to the comparably larger size of the particles observed right after injection (see figure 5b). After injection, the amount of available precursor will be relatively small, leading to a slower growth and a minimal focusing of the size distribution. The lacking onset of Ostwald ripening could be due to the following reason: Ostwald ripening takes place when the supersaturation falls under a certain threshold. The use of a heterogeneous precursor (PbCl$_2$) should maintain the concentration of ‘solubilized’ cationic precursor constant throughout the reaction. The decrease in supersaturation has thus to be attributed to the decrease in the sulphur concentration, especially considering that sulphur is the limiting reagent. The heterogeneous nature of PbCl$_2$ will thus not completely prevent Ostwald ripening from happening, but it will delay it substantially by maintaining the concentration of one precursor constant. It is plausible in fact, as shown in figure 5b, that the large increase in peak wavelength at the very last stage of the reaction for the low concentration case is due to the eventual onset of Ostwald ripening.

One can argue that similar conditions should be available in the case that the Pb precursor would be soluble, since it is not the limiting reagent. In such a case, its decrease in concentration during the reaction could also be considered negligible. However, a soluble precursor would be completely available to react and would contribute to the supersaturation in its entirety. A soluble lead precursor in similar concentrations would then result in the formation of a much larger number of nuclei during injection owing to the much higher supersaturation, and a consequent much faster depletion of the limiting reagent, much like that observed in normal homogeneous nanocrystal syntheses.

Heterogeneous conditions result in smaller supersaturation of available precursors, especially at the time of injection. This is reflected in the difficulty of generating very small (2–3 nm diameter) PbS nanocrystals by using PbCl$_2$ in oleylamine. PbS nanocrystals can be easily produced in the approximately 2–3 nm range using homogeneous reactions (Hines & Scholes 2003), while the smallest size we could achieve with PbCl$_2$ is approximately 4.5 nm (Cademartiri et al. 2006b). Considering the effect of size on the properties of these particles, one can understand how this can be a very serious limitation. As it was later found, this aspect can be addressed by choosing the right precursor, and ultrathin structures have been synthesized by heterogeneous syntheses (Cademartiri et al. 2008b).

Another consequence of the lower concentrations of available precursors is that the growth rate is moderated during the whole growth phase, yielding less defective structures at lower temperatures. The influence of growth rate on defect concentrations is a widely studied topic in crystal growth (Scheel & Capper 2008). Heterogeneous reactions are generally performed at temperatures that are milder (100–240°C) than most organometallic nanocrystal syntheses (often above 300°C).
Another important aspect of this reaction that highlights the differences between heterogeneous and homogeneous reaction schemes for the synthesis of nanocrystals is its influence on the structure and composition of the surface of the nanocrystals. An XPS analysis of our PbS nanocrystals obtained from PbCl₂ revealed a sizeable amount of chloride ions on their surface, even after extensive purification procedures (Cademartiri et al. 2006a). These ions are strongly bound and can be removed by reaction of the nanocrystals with oleic acid. The amount of chloride we measured was consistent with a monolayer-thick corona of PbCl₂ on the surface of the PbS nanocrystals. XRD analysis proved that the measured chloride was not in a crystalline form, thus excluding the presence of colloidal PbCl₂ impurities. These results were recently confirmed by Hens’s group at the University of Ghent (Moreels et al. 2009).

We think this is a remarkable finding for two main reasons. Firstly, efforts to coat lead chalcogenide nanocrystals with a well-defined and reproducible shell of an insulator had been very scarcely successful. This has always been a main limitation in the use of these particles in (i) biological experiments, owing to the sensitivity of chalcogenides to hydrolysis, and (ii) dried conditions, owing to the sensitivity of lead chalcogenides to oxidation. The presence of a PbCl₂ shell seems to be mostly responsible for the remarkable resilience to oxidation of these PbS/PbCl₂ nanocrystal quantum dots. This resilience allows them to retain their luminescence even after being exposed to air plasma, which quantitatively removes all their ligands and oxidizes their surface (Cademartiri et al. 2005, 2008a). Secondly, the presence of a strongly bound chloride shell on the surface places some strong and informative constraints on how we can describe the reaction mechanism by which these particles form. Considering the organic environment and the strong bond between Pb²⁺ and Cl⁻, it is implausible that free Cl⁻ ions would adsorb to the nanocrystal surface after their growth had ended. It is further implausible that PbCl₂ nanocrystals would precipitate on the PbS nanocrystal surface upon the cooling down of the reaction mixture, as this would lead to (i) a thicker shell, which would have been detected from microscopy studies and from the relation between size and emission wavelength, or (ii) the formation of a sizeable amount of a crystalline phase of PbCl₂ that was not observed by XRD. This leads us to the conclusion that the chloride ions that end up on the surface are most likely accompanying a Pb²⁺ cation during the whole course of the reaction, from the solid PbCl₂ to the solubilized intermediate moiety, which then reacts with the S precursor. The outermost layer of Pb atoms will not be forced to release the chloride counter ions until further reaction with S precursors. The excess of Pb precursors would ensure that any sulphur at the surface is capped by a Pb²⁺ counter ion. This would result in a surface substantially enriched with lead ions, as experimentally observed by two independent laboratories (Cademartiri et al. 2006a; Moreels et al. 2007, 2009). Such enrichment is usually prevented by the absence of a shielding counter ion: a Pb²⁺-terminated surface will be strongly charged, unless a counter ion is shielding it. Amines are not expected to work as counter ions, but rather as coordinating ligands. The predicted (and reproducibly observed) substantial enrichment of the surface with Pb ions can thus only be explained with chlorides sitting on the surface. There are a series of energetic considerations that further support this picture. An unscreened charged surface is more energetic than a screened one. But, as mentioned, the reaction takes place in the absence of suitable counter
ions, with the exception of chlorides. The advantage of chlorides is that they are monovalent and are thus perfectly fit to charge-compensate a surface bivalent ion such as \( \text{Pb}^{2+} \). A bivalent counter ion would in fact just switch the sign of the surface charge and thus would be less efficient at reducing the surface energy.

These arguments are, at the moment, still speculative. The data collected so far do not allow for a more substantiated discussion. One of the weaknesses of nanochemistry as a field has been the lack of the kind of quantitative studies that would give a foundation for a comprehensive understanding of nucleation and growth in these systems (Ozin & Cademartiri 2009). More exploratory studies have generally been preferred. To a certain extent, there is nonetheless value to postulated mechanistic hypotheses as long as they are chemically sensible, verifiable and lead to clear predictions.

These considerations give us suggestions on the nature of the solubilized precursor, which should be in the form of a complex (or cluster) that includes a \( \text{PbCl}_2 \) stoichiometry and that is stabilized in solution by coordination of amines. These moieties could be considered as precursors but also as embryos, if we follow a traditional inorganic colloid chemistry terminology (Matijevic 2007). These embryos would then coalesce, via a condensation mechanism, to form the nuclei. Small clusters or molecular aggregates (dimers, trimers, etc.) have been previously observed in halide salts (Huber et al. 1974). Such structures could constitute the basis of our understanding of the intermediate stages of these reactions. These results highlight how these heterogeneous strategies can cause not only different growth kinetics, which, if optimized properly, can lead to smaller polydispersity, but also a different surface chemistry, with plausible repercussions on the way we can think of and use these structures for catalytic, sensing or device-oriented applications.

One of the least favourable aspects of this \( \text{PbCl}_2\)–\( \text{S}\)–OLA reaction involved the purification of the product from the solid \( \text{PbCl}_2 \). While one would think that \( \text{PbCl}_2 \) could be easily removed by centrifugation, this is only partly the case. A large amount of \( \text{PbCl}_2 \) is left in the solution in the form of stable nanocrystalline colloids. The long-term colloidal stability of these impurities is much inferior to that of the product (which shows hardly any precipitation or aggregation, even after years in solution). This results in a slow precipitation of \( \text{PbCl}_2 \) powder that can take months to complete (Cademartiri et al. 2006).

This is not a general characteristic of heterogeneous reactions, but is observed with certain precursors. The precipitation of the impurity can be selectively triggered by the use of a suitable quantity of the appropriate non-solvent. In the case of this reaction, small amounts of acetone were found to destabilize and precipitate all \( \text{PbCl}_2 \) colloids, while leaving the \( \text{PbS/\text{PbCl}_2} \) nanocrystals in solution. A further addition of acetone can precipitate the product, while leaving the sulphur precursor in solution, avoiding the previous limitations.

A similar strategy was used to synthesize \( \text{Bi}_2\text{S}_3 \) nanodots and nanorods by reacting \( \text{BiCl}_3 \) with \( \text{S} \) in oleylamine (Malakooti et al. 2006). Bismuth chloride, just like lead chloride, is not soluble in oleylamine, but rather forms a slurry. The injection of the sulphur solution was performed at 170°C, while growth was allowed to proceed at 130°C.

Figure 6a,b shows, respectively, \( \text{Bi}_2\text{S}_3 \) nanodots and nanorods that could be obtained from this reaction. These different shapes could be obtained selectively by changing the ratio between bismuth chloride and sulphur. Nanodots would
form in excess of bismuth, while nanorods would form in excess of sulphur. While the exact reason for this difference is not fully understood, it is worth noting that this was the first report of spherical Bi$_2$S$_3$ nanocrystals. All other reports in the literature on this compound, as far as we know, describe nanostructures that are elongated along the (001) direction. The origin of this preferred anisotropy is plausibly associated with the anisotropic Bi$_2$S$_3$ lattice and the unit cell. The structure of Bi$_2$S$_3$ is composed of buckled ribbons with a Bi$_2$S$_3$ stoichiometry and stretching along the c-axis of the unit cell. The bonds within these ribbons are covalent, while the ribbons are interacting with each other via weaker forces (primarily ionic and van der Waals).

In order to understand the origin of the spherical morphology, we propose an explanation that is related to the heterogeneous nature of the reaction. The BiCl$_3$/oleylamine mixture is hydrolysed in the presence of moisture to BiOCl. This intermediate is then reduced to metallic bismuth while the primary amine in oleylamine is oxidized to a nitroso group. The presence of nitroso groups was confirmed by XPS (Malakooti et al. 2006). This mechanism was further confirmed by the darkening in colour of the BiCl$_3$ dispersion in oleylamine.
prior to the injection of sulphur. This darkening did not occur when the reaction was performed under an inert atmosphere. It is then plausible that metallic Bi nanocrystals are formed from the reduction of BiOCl and are then sulphidized upon the injection of sulphur. Sulphidation has been widely used to transform oxidic and metallic structures and nanostructures to the sulphide analogue. The shape of the nanoscale bismuth metal is generally spherical. Oleylamine has been previously used to coordinate the surface of metal nanoparticles and control their growth. The reason why this process happens only with an excess of bismuth precursor seems to us to be related to supersaturation. In excess of bismuth, the injection of sulphur might not increase the supersaturation of soluble precursors enough to lead to the formation of stable Bi₂S₃ nuclei from a homogeneous reaction between a solubilized bismuth precursor/intermediate and the sulphur precursor. This would mean that S could still react with Bi in a heterogeneous way, by sulphidizing a solid bismuth particle. Sulphidization products largely retain the shape of the reactant solid, and, considering that metallic bismuth particles are spherical, this could explain the formation of spherical nanocrystalline Bi₂S₃. In the case of sulphur excess, the concentration of dissolved sulphur and molecularly dissolved bismuth species could be instead large enough to result in the formation of Bi₂S₃ nuclei, which could then grow in a more conventional epitaxial way, leading to the preferred elongated shape.

From a chemistry point of view, this work demonstrates that heterogeneous reactions can cause not only different growth kinetics by modulating the availability of the solubilized precursor, but also entirely different mechanisms of growth, which are inherently heterogeneous.

The work on heterogeneous strategies on the Bi₂S₃ system lead us then to the discovery of a novel kind of nanostructure (Cademartiri & Ozin 2009a,b). By replacing BiCl₃ with the more stable bismuth citrate, and by developing a different set of experimental conditions, we obtained Bi₂S₃ nanowires of ultrathin (less than two unit cells) diameter (Cademartiri et al. 2008b). These nanowires were discovered to be polycrystalline, 1.6 nm wide and several microns long.

Figure 7 shows a representative TEM image of Bi₂S₃ nanowires drop-cast on a carbon-coated grid. The wires were synthesized by a hot injection method. A room temperature solution of S in oleylamine was swiftly injected in a dispersion of bismuth citrate in oleylamine at 130°C. The limiting reagent was bismuth citrate; conditions of excess bismuth led to the formation of large Bi₂S₃ nanorods of rather inhomogeneous size. The nanowires showed the first evidence of excitonic peaks at room temperature in Bi₂S₃ and a remarkably large extinction coefficient (figure 7b,c).

The mechanism of growth of these structures is still under investigation, but the most interesting aspect is that their growth, in spite of their polycrystallinity, appears to occur only in one direction, as demonstrated by the invariance of their diameter with growth time. Polycrystalline nanostructures are generally growing in a near isotropic way. The anisotropic growth of polycrystalline materials is generally due to a templating mechanism.

Similar structures have been obtained previously via oriented attachment of single crystalline spherical units. This usually, but not always (Penn & Banfield 1998), leads to a single crystalline nanowire geometry (Pradhan et al. 2006),
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Figure 7. Bismuth sulphide ultrathin nanowires obtained by reacting a bismuth citrate slurry in oleylamine with sulphur. (a) TEM image of Bi$_2$S$_3$ ultrathin colloidal nanowires; (b) UV-VIS absorbance spectrum of a colloidal dispersion of Bi$_2$S$_3$ ultrathin nanowires and its second derivative that highlights the three excitonic transitions; (c) the per cation extinction coefficient of the Bi$_2$S$_3$ ultrathin nanowires (calculated from TGA and ICP measurements), compared with the analogous quantity for PbS nanocrystal quantum dots. (a) Scale bar, 200 nm. (c) Solid line, PbS quantum dots; dashed line, Bi$_2$S$_3$ nanowires (ICP); dotted line, Bi$_2$S$_3$ nanowires (TGA).

that is different from what was observed in these wires. The polycrystallinity of these ‘necklace’ nanowires seems to be responsible for their remarkable apparent flexibility, which is the object of the current investigation.

4. Conclusions

The recent work described in this perspective has demonstrated that sparingly soluble precursors can be used for the synthesis of nanoscale colloids. While this might have initially looked like an incremental departure from the established homogeneous reaction schemes and unlikely to bear fruit, it is now clear that the differences are fundamental and relevant and the opportunities for making new and improved nanomaterials are considerable.

— The choice of precursor has been dramatically extended, from a rather minute number of organometallic compounds that are soluble in organic solvents and ligands to the large majority of inorganic solids that form...
suspensions. These compounds, often minerals, have the advantage of being cheaper, much less toxic and much more stable than soluble organometallic compounds.

— These reactions are much more easily scalable since (i) the solid state of the precursor in solution allows for its easy recovery at the end of the reaction, (ii) the growth temperatures are milder, (iii) the growth kinetics are slower, putting fewer constraints on the necessary speed of injection and mixing, and (iv) the initial concentration of solid precursors can be large, given their stability and low solubility.

— The growth kinetics is vastly different from a standard homogeneous reaction since the presence of the solid precursor maintains the concentration of available solubilized precursor constant. This effectively prolongs the duration of the focusing regime and substantially delays the onset of Ostwald ripening.

— The heterogeneous nature of the reaction mixture can result in the observation of different growth mechanisms, leading to new or unexpected nanoscale shapes and phases.

These very exciting aspects of this reaction scheme come with challenges related to the understanding of the chemical nature and reactivity of the available precursors, as well as with the understanding of the role of the new parameters (such as particle size, faceting, etc.) introduced by the presence of a solid phase.

It is our belief that these complications make these heterogeneous synthetic routes to new nanomaterials even more interesting and filled with promise for discovery and invention.

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