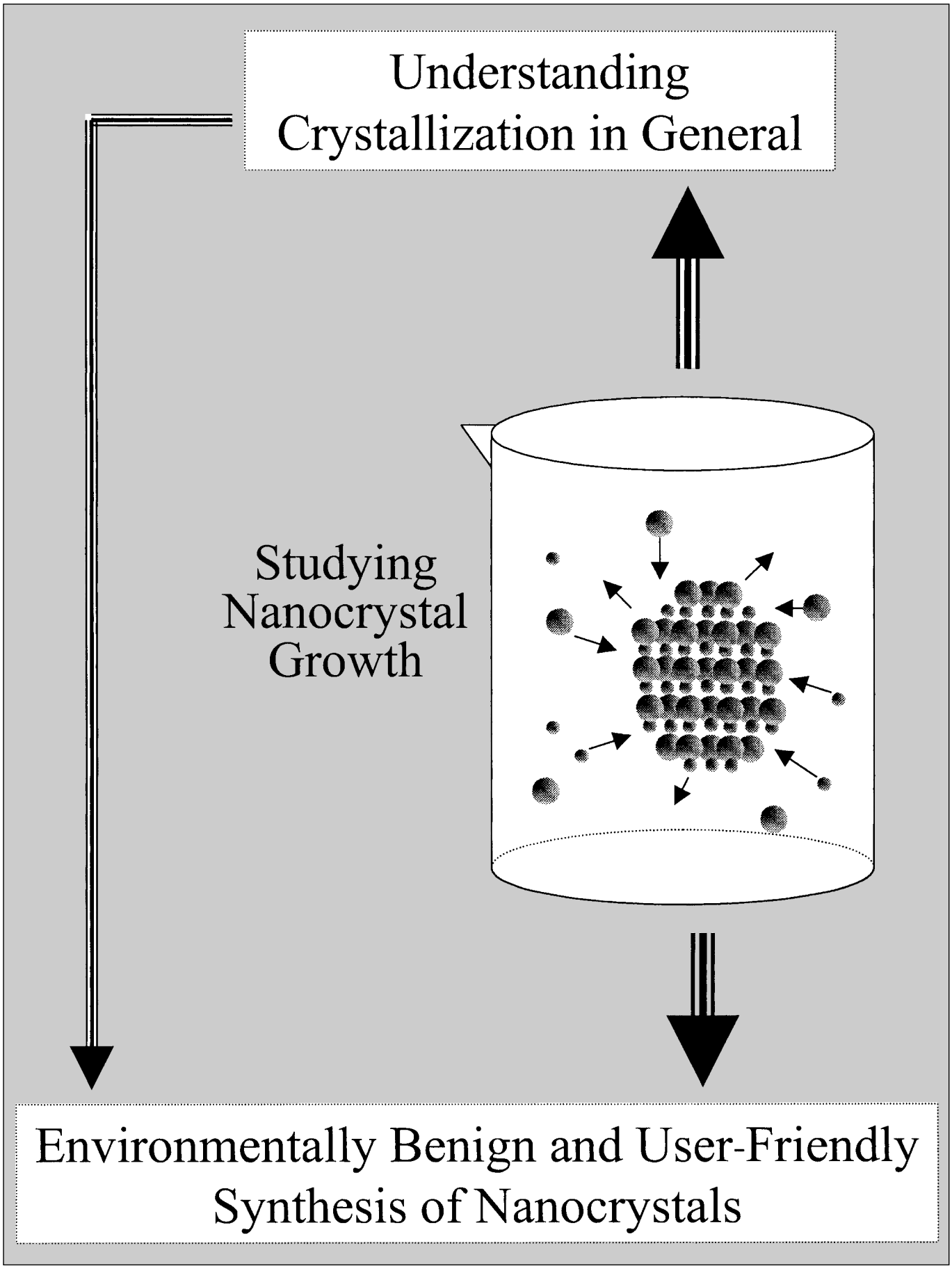

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Green Chemical Approaches toward High-Quality Semiconductor Nanocrystals

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Abstract: Green chemistry principles have gradually been implemented into the development of the synthetic chemistry of high-quality semiconductor nanocrystals.[1, 2] In comparison with the original organometallic approach, the resulting alternative routes are safe, simple, inexpensive, reproducible, versatile, "user friendly", and yield nanocrystals with well-controlled size, shape, and size/shape distribution. Further developments in this direction will promote the understanding of crystallization in general.

Keywords: colloids · green chemistry · nanocrystals · synthesis design

Background

Colloidal semiconductor nanocrystals, also known as colloidal quantum dots/rods, nanoparticles, and nanoclusters, are nanometer-sized fragments of their corresponding bulk crystals.[3–5] Since we are dealing with crystallites with a variety of shapes and sizes in this article, "nanocrystals" is probably the best term and will be used exclusively. The interesting size-dependent properties of semiconductor nanocrystals, especially their optical properties, have attracted much attention both in fundamental research and technical applications in recent years. At present, access to nanocrystals of the desired quality substantially limits the development of the field.

A successful synthetic scheme should, at the least, produce highly crystalline nanocrystals with close to monodisperse size distribution if one wants to exploit their size-dependent properties. The ability to vary the size and shape of the resulting nanocrystals is an additional measurement of such a synthetic scheme. Presumably, control over the optical and/or other properties in which you are interested is also an important concern. To reach these standards, the synthesis of CdSe nanocrystals by using dimethyl cadmium, $Cd(CH_3)_2$, as the cadmium precursor in technical-grade trioctylphosphine oxide (Tech TOPO) or in pure TOPO with some additives, which are mainly analogues of the impurities in Tech TOPO, was the best up until the year 2000.[6–9] After this organometallic approach was introduced in the early 90s,[9, 10] this synthetic scheme was considered to be an inspiring example and model system in the field. However, the organometallic synthetic approach in coordinating solvent possesses several intrinsic disadvantages. The raw materials, especially the organometallic precursors, are extremely toxic, expensive, unstable, explosive, and/or pyrophoric; therefore sophisticated equipment, such as a glovebox equipped with a refrigerator, and an inert atmosphere are required. Secondly, the reactions are not easy to control or reproduce. Finally, the organometallic approach has not generated any other type of semiconductor nanocrystal with comparable quality to that of the CdSe nanocrystals.

Green chemistry[11] or environmentally benign chemistry is a general term for a group of concepts used in the synthesis and manipulation of chemicals that have been applied almost exclusively to organic synthesis. The main goal of green chemistry is to develop environmentally benign chemical methodologies and to minimize the damage to the environment by human activities. The following concepts are related to the current development of synthetic chemistry for high-quality colloidal nanocrystals.

1) *Alternative routes.* Chemistry as a major branch of science and industry has been in place for hundreds of years. Countless procedures have already been developed for the production and processing of a large variety of chemicals. Unfortunately, many of them generate a lot of pollutants; this has caused serious public concern. For the sake of the environment, these procedures should be re-evaluated and redeveloped to eliminate any unnecessary toxic raw materials and side products, and any operations that are harmful to the workers. In addition, alternative routes should include less expensive and simpler approaches. In general, alternative routes can be implemented in a step-by-step manner so as to eventually become environmentally benign.
2) *Diversity.* Evidently, if a procedure can be applied to the production/processing of many different types of products

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with only small variations in the conditions and equipment the procedure should be very valuable. Importantly, all the products should be as pure as desired and should not require complicated and tedious separation procedures, such as chromatography.

3) *Atom economy.*[12] It is important to consider the consumption of raw materials and energy and the generation of waste when a new chemical procedure is designed, no matter whether it is an original one or an alternative approach. The ideal case is 100% conversion of all the starting materials added to a reaction flask with no by-products. Normally, the generation of water or some types of harmless salts, such as NaCl, is acceptable. If the starting materials, including solvents, can be recycled with ease, the procedure is also compatible with atom economy.
4) *User-friendly chemistry.* In certain fields, most scientists and engineers are not synthetic experts and like to adopt "user-friendly" synthetic protocols. The field of colloidal semiconductor nanocrystals as an interdisciplinary and rapidly developing subject is more or less in this line. Most research groups are interested in the properties and applications of these novel materials and possess a lot of expertise in the fields of fundamental and device physics, physical chemistry, biological sciences, etc. They prefer to be the users of easily-adoptable synthetic schemes, instead of the developers of their own synthetic methods.

I think the concept of "user-friendly chemistry" is probably the difference between the traditional green chemistry and the green chemical synthesis in the field of colloidal nanocrystals. Therefore, green chemical approaches for colloidal nanocrystals should not only be environmentally benign but also user friendly. As I will discuss below, the final nanocrystal products can be quite toxic. In this sense, green chemistry refers to the procedures of the synthesis and processing instead of the final products.

Experimental Feasibility

Although high quality semiconductor nanocrystals have been in ever higher demand in recent years, the organometallic approach for the synthesis of high-quality CdSe nanocrystals has only been adopted by a limited number of research groups around the world because of the requirements of the equipment and settings. This led to a natural thought—to seek easily adoptable or user friendly synthetic schemes for semiconductor nanocrystals. There are numerous reports regarding the synthesis of CdSe nanocrystals in water by using inorganic cadmium salts as the cadmium precursor. However, the quality of the nanocrystals resulting from those synthetic methods in aqueous solutions is not nearly as good as that of the CdSe nanocrystals synthesized by the organometallic approach. One reason could be that the temperature that can be achieved in water is significantly lower than the typical reaction temperatures (200–360 °C) used in the organometallic approach. It is common sense that high-temperature processes yield crystals with better crystallinity, although it is not well-documented in the field of colloidal nanocrystals.

To our minds, the alternative routes must be at least as good as the traditional organometallic approach in all aspects, but with safe and inexpensive raw materials, which do not subsequently require any sophisticated equipment and procedures. A reasonable thought on this direction is to gradually deviate from the original organometallic approach. As the first step, we chose to replace dimethyl cadmium, which is certainly the least desirable chemical among all the starting materials and products. To do so, we had to figure out the role of dimethyl cadmium in the traditional organometallic approach.

Experimental results told us that there must be sufficient amounts of cadmium molecular species not in the form of nanocrystals in the reaction solutions to suppress Ostwald and intraparticle ripening in the entire growth process of a typical organometallic synthesis.[6, 8] A typical synthetic reaction that uses the traditional organometallic approach normally lasts for minutes to hours at elevated temperatures. Evidently, $Cd(CH_3)_2$ cannot survive such a process, since it even decomposes at room temperature and has to be stored in a refrigerator in a glovebox.

A series of experiments was designed to study the fate of $Cd(CH_3)_2$ after it has been introduced into the reaction flask at high temperatures. The results revealed that metallic cadmium precipitated immediately after the injection of $Cd(CH_3)_2$ into pure TOPO at high temperatures. However, $Cd(CH_3)_2$ was stabilized by the presence of hexylphosphonic acid (HPA), an analogue of the key impurity in Tech TOPO. The number of moles of HPA must be at least equivalent to that of $Cd(CH_3)_2$ in order to obtain an optically clear solution. After purification, the soluble cadmium compound was proven to be a Cd–HPA complex.[6] Synthesis with the purified complex indeed generated CdSe nanocrystals with comparable quality to those of the CdSe nanocrystals synthesized by the traditional organometallic approach.[1, 6]

Current Status

Experimental results indicate that the Cd–HPA complex can be formed in situ by the reaction of cadmium oxide and HPA in pure TOPO at elevated temperatures.[1] High-quality CdSe nanocrystals were formed after injection of a selenium–organophosphine solution into the Cd–HPA complex solution formed in situ in hot TOPO. Apart from the tremendous advantages of cadmium oxide over dimethyl cadmium, this alternative scheme is capable of producing monodisperse CdSe nanocrystals in a size regime smaller than 2 nm; this is not easy to achieve with the traditional organometallic approach. However, with this very first alternative route it is not easy to produce large particles. For the original organometallic approach, relatively large-sized nanocrystals are produced by multiple secondary injections of the precursors into the reaction flask.

Fortunately, most recent studies indicate that HPA and CdO are not unique. Fatty acids, amines, other phosphonic

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acids, and phosphine oxides can all serve as the ligands/solvents for the synthesis of high-quality CdSe nanocrystals. The inorganic and organic salts of cadmium with an anion from a weak acid, such as $CdCO_3$ and cadmium acetate, can all be used as cadmium precursors. As a result, hundreds of possible combinations of ligands/solvents/precursors can suddenly be realized for designing a rational alternative route for different purposes. In contrast, the traditional organometallic approach was mainly limited to $Cd(CH_3)_2$ and Tech TOPO for years.

Today, about one year after the discovery of the first alternative approach based on the replacement of $Cd(CH_3)_2$ by CdO, the alternative routes have shown superior abilities in all aspects than the traditional $Cd(CH_3)_2$ approach that has existed for more than 10 years. For example, nearly monodisperse CdSe nanocrystals have been synthesized in a much larger size range, from about 1.5 nm to 25 nm, through alternative routes without using secondary injections (Figure 1, left).[2] The shape control of the resulting CdSe nanocrystals is certainly better than that with the traditional organometallic approach (Figure 1).[13] The nanocrystals as prepared are nearly monodisperse, with 5–10% relative standard deviation, and thus size sorting is not necessary for most purposes. The photoluminescence quantum efficiency of the as-prepared CdSe nanocrystals can reproducibly reach as high as 85%,[14] which is much higher than any reported values for CdSe nanocrystals prepared by the older method.

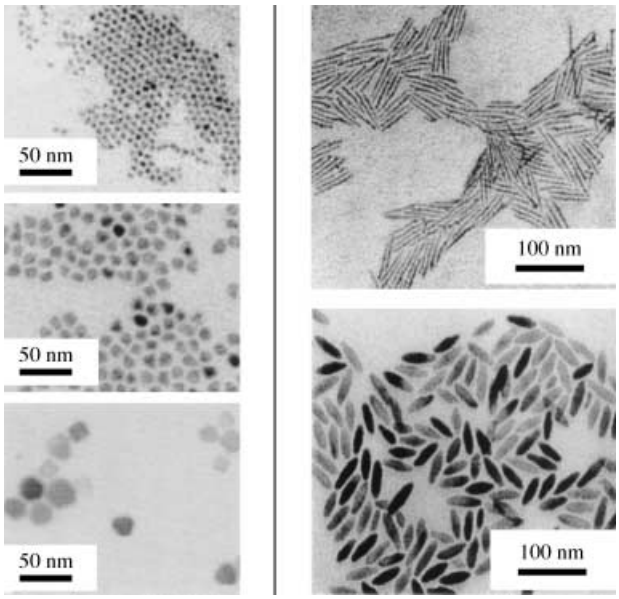

Figure 1. Transmission electron microscope (TEM) images of size- and shape-controlled CdSe nanocrystals synthesized by greener approaches. All the samples are as prepared and no additional size-/shape-sorting procedures were applied.

The quality of the as-prepared CdSe nanocrystals synthesized by the alternative routes can be considered to be a result of the relatively simple nucleation and growth path in the solution. As discussed above, dimethylcadmium is very unstable at elevated temperatures. After it has been injected into the hot reaction mixture, some of the molecules of this active organometallic compound react with selenium precursors and form CdSe nuclei, while some of them are converted to more stable complexes. If conditions allow, these newly formed complexes can also take part in the formation of nuclei. For the same reason, the following growth process may also involve multiple cadmium sources. As a result, the control of such a system is likely to be more complicated than a simple alternative route.

It is documented that the monomer concentration in solution is a key factor in determining the shape of the resulting CdSe nanocrystals.[6, 13] Since rod-, rice-, and branch-shaped CdSe nanocrystals possess higher free energy than nanocrystals with a dot shape, higher monomer concentrations are required throughout the entire growth process for the growth of these elongated nanocrystals. In fact, it was observed that these elongated nanocrystals are converted to dot-shaped ones at relatively low monomer concentrations.[6, 13]

The exceptional diversity of the products of the alternative routes is further demonstrated by the synthesis of high-quality CdTe and CdS nanocrystals.[1] In terms of the control over their size, shape, and size/shape distribution, the as-prepared CdTe nanocrystals shown in Figure 2 are comparable to those of the CdSe nanocrystals synthesized by the traditional organometallic approach and much better than the CdTe nanocrsytals synthesized by any other means.

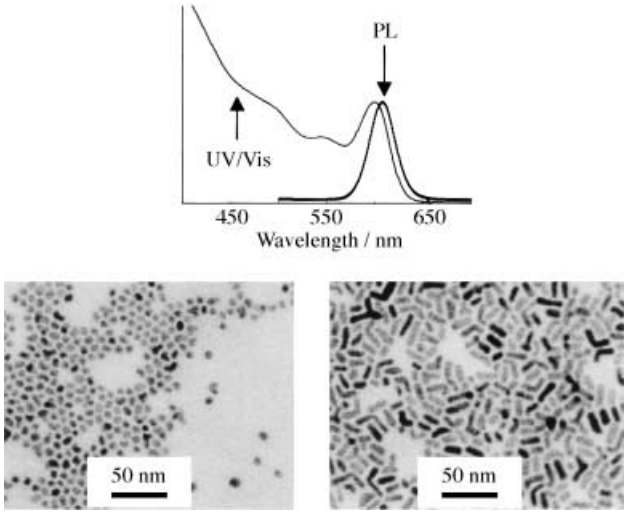

Figure 2. UV/Vis absorption and photoluminescence (PL) spectra (top), and TEM images (middle and bottom) of CdTe nanocrystals synthesized by using CdO as the cadmium precursor. All the samples are as prepared and no addition size-/shape-sorting procedures were applied.

Evidently, these alternative routes are significantly more user friendly than the traditional organometallic approach. The alternative routes discussed above can be readily performed in a regular fume hood without using a glovebox. This, along with the low-cost and safe raw materials, should provide access to these green chemical approaches to nearly any scientific units who are interested in studying these novel materials.

Besides us, several groups have been trying to develop alternative variations of the original organometallic approach, which are performed by using relatively safe single precursors.[15, 16] For this approach, single precursors containing both cadmium and selenium have to be synthesized separately and, to our knowledge, this prior synthetic step has always involved some toxic chemicals and additional procedures. In addition, it is not easy to vary the ratio between the two monomers; this may play a critical role in designing an optimal synthetic scheme.[8] Overall, the development of this direction is not as advanced as the ones that use separate precursors discussed above.

Remaining challenges and opportunities

The diverse alternative routes for the synthesis of high-quality cadmium chalcogenide nanocrystals discussed above have improved the synthetic chemistry of those types of semiconductor nanocrystals in a revolutionary way. However, there is still some room for improvement as far as green chemistry is concerned. For example, the selenium and tellurium precursors being used are closely related to organophosphorus compounds that are not very "green" at all,[1] although we did discover some green sources for sulfur precursors for the synthesis of CdS, ZnS, and other sulfide semiconductor nanocrystals. It should be mentioned that the potential replacements of these organophosphorus-related precursors should not be synthesized/derivatized from any chemicals with similar toxicity to organophosphorus.

Atom economy has not yet played a role in the development of alternative routes. This is certainly an important direction to pay attention to. In principle, it is impossible to obtain 100% conversion of the raw materials to high-quality semiconductor nanocrystals. Some excess precursors/monomers must exist in the growth solution in order to suppress Ostwald and intraparticle ripening.[6, 8] As a result, one has to develop an easy way to recycle the raw materials; this in turn requires a full analysis of the products and by-products of a growth reaction. To our knowledge, this has never been performed and may not be a trivial task. Nevertheless, this is often the situation for the development of colloidal nanocrystal chemistry: a lack of fundamental knowledge in general. That is why we have always carried out mechanism studies along with the development of better synthetic and processing methodologies.[6, 8, 13, 17]

The synthetic chemistry for other types of semiconductor nanocrystals is noticeably less developed than that for cadmium chalcogenides at present. It is our intention to extend the newly learned knowledge of the model systems to the development of synthetic chemistry based on green chemistry concepts for other types of semiconductor nanocrystals, more broadly speaking, colloidal nanocrystals/nanoparticles. These new systems may have many known and possibly unknown advantages over cadmium chalcogenides nanocrystals in certain aspects.

It is debatable whether a synthetic scheme for making cadmium-related compounds can be classed as a green chemical approach, because cadmium is intrinsically quite toxic. Traditionally, green chemical synthesis does not mean that the targeted products are not toxic.[12] Instead, its emphasis is on the starting materials, the procedures, the side products, the energy consumption, and the simplicity of the equipment. To this standard, the related alternative routes for the synthesis of cadmium-related semiconductor nanocrystals can be considered as green chemical approaches, or at least, as "greener approaches". Eventually, the field may have to find some alternative semiconductor compounds to replace cadmium-related ones. Some types of III–V semiconductor nanocrystals, such as InP and GaAs, may have similar optical properties to CdSe and CdTe nanocrystals. However, most of the III–V compounds are more or less as toxic as the cadmium compounds.

Significance

The practical significance of green chemical approaches for the synthesis of semiconductor nanocrystals is obvious. The fundamental payoff may be visualized by the comparison between this movement and the total synthesis of natural products in the field of organic chemistry. In the latter case, all the products are already known, and the total synthesis does not make chemically new products. However, the organic chemistry knowledge built up around it and the understanding of natural/biological processes are undoubtedly important. For people working on developing green chemistry of nanocrystal synthesis, the fundamental significance may appear as the ultimate understanding of crystallization in general, which has amazed and puzzled human beings for thousands of years. There are two reasons to support such a hypothesis. First of all, any crystallization process is initiated and determined by the formation of nanosized species, so-called nuclei. Secondly, the thermodynamic driving force for crystallization is to minimize the total surface energy of the system, which is significant (among the total free energy of the system) and varies dramatically only in the nanometer size regime (Figure 3). This implies that it should be the right rationale to seek in the nanometer regime for the answers to the mysterious phenomena of crystallization.

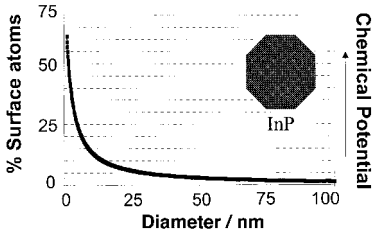

Figure 3. The surface-to-interior atom ratio and chemical potential of differently sized crystals in nanometer regime. Approximately spherical InP nanocrystals are used as the example.

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