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Band Gap and Composition Engineering on a Nanocrystal (BCEN) in Solution

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CONSPECTUS

Colloidal nanocrystals with "artificial" composition and electron band structure promise to expand the fields of nanomaterials and inorganic chemistry. Despite their promise as functional materials, the fundamental science associated with the synthesis, characterization, and properties of colloidal nanocrystals is still in its infancy and deserves systematic study. Furthermore, such studies are important for our basic understanding of crystallization, surface science, and solid state chemistry.

"Band gap and composition engineering on a nanocrystal" (BCEN) refers to the synthesis of a colloidal nanocrystal with composition and/or electron energy band structure that are not found in natural bulk crystals. The BCEN nanostructure shown in the Figure includes a magnetic domain for the separation and recycling of the complex nanostructure, a photoactivated catalytic center, and an additional chemical catalytic center. A thin but porous film (such as a silicate) might be coated onto the nanocrystal, both to provide chemical stability and to isolate the reaction processes from the bulk solution. This example is a catalytic complex analogous to an enzyme that facilitates two sequential reactions in a microenvironment different from bulk solution.

The synthesis of colloidal nanocrystals has advanced by a quantum leap in the past two decades. The field now seems ready to extend colloidal nanocrystal synthesis into the BCEN regime. Although BCEN is a very new branch of synthetic chemistry, this Account describes advances in related synthetic and characterization techniques that can serve as a useful starting point for this new area of investigation.

To put these ideas into context, this Account compares this new field with organic synthesis, the most developed branch in synthetic chemistry. The structural and functional diversity of organic compounds results from extending design and synthesis beyond the construction of natural organic compounds. If this idea also holds true for inorganic nanocrystals, "artificial" BCEN nanocrystals will most likely outperform the inorganic nanocrystals with naturally occurring structure and composition. If the importance of artificial molecules is a positive lesson from organic synthesis, the practical disadvantage of organic chemistry is that purification can prove much more time consuming than the reaction itself. To get around this problem, colloidal nanocrystal chemists can attempt to avoid these potential purification challenges in the early stages of synthetic method development.

1. Introduction

"Band gap and composition engineering on a nanocrystal" (BCEN) refers to synthesis of a colloidal nanocrystal with designed composition and electron energy band structure that do not occur in natural bulk crystals. Simple examples of such nanocrystals include a core/shell nanocrystal,[1] a core with multiple shells,[2] a heterodimer with two composition domains,[3] and a doped nanocrystal.[4] Such unique structures enable the nanocrystal to possess either unique properties or multiple functions. One example of BCEN nanocrystals with unique properties is doped colloidal quantum dots (d-dots),[5] which offer a class of nanocrystal-based emitters with minimum reabsorption, outstanding thermal stability, high emission quantum yield, no Class A heavy metals, and yet tunable emission wavelength. A simple example of multiple functional nanocrystals is a het-

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erodimer nanocrystal with a magnetic domain and one semiconductor domain.[3]

The central task of BCEN is to bring in “structure-dependent properties” and “composition-dependent properties” for colloidal nanocrystals, in addition to their well-recognized “size-dependent properties”. Chemistry of BCEN is to design, synthesize, and characterize the needed nanostructures for realization of “structure-dependent properties” and “composition-dependent properties”, and also partially recast “size-dependent-properties”. Different from band gap engineering on bulk solid substrates, BCEN will be performed in solution and the resulting products shall be processable using standard solution techniques. Further apart from band gap engineering on bulk solid substrates, BCEN might not limit itself to semiconductors.

BCEN shall start from nanocrystals with simple compositions, such as the core nanocrystals for core/shell growth. This Account, however, shall not deal with the synthetic chemistry of those simple nanocrystals, on which an essay was published recently to reflect the personal assessment on that subject from the author.[6]

2. Inorganic Nanocrystals Verses Organic Molecules

Although broad interest of colloidal nanocrystals in chemistry, physics, biology, and engineering can be somewhat justified fundamentally, their potential applications as various functional materials are likely more compiling, provided the tight demand of natural resources at present. Their size-dependent properties and solution-based processability are two well-known unqiue features,[6] which may make inorganic compounds be as diverse, if not more diverse, as organic ones. For organic compounds, some small variation in size has been viewed as a totally different molecule, such as methanol verses ethanol, which could be regarded as some kind of recognition of “size-dependent properties”. However, the properties of inorganic crystals were historically not considered as size-independent. For example, there was barely any concern about the chemical properties of sodium chloride crystals with 1000 NaCl units versus those with 2000 NaCl units. In this sense, the discovery of size-dependent properties of inorganic nanocrystals[7] bring inorganic chemistry one step closer to the status of modern organic chemistry.

A critical step for organic chemistry to become as diverse as it is today is the synthesis of unnatural organic compounds. Similarly, if colloidal nanocrystals are limited to naturally occurring crystals, the available products will unlikely match the needs of functional materials. From a different perspective, organic synthesis in many ways has been incorporating different functional groups into a single molecule. BCEN is evidently the means for scientists to do the same for nanocrystals, yielding nanocrystals with unique properties due to their unnatural structure and/or composition.

Band gap engineering was originally a term in the field of semiconductor science and engineering,[8] which refers to artificial control of the electron energy band structure in a semiconductor crystal. The most well-known structures are semiconductor quantum wells, which are the basic structures for light-emitting diodes, solar cells, and semiconductor lasers. Band gap engineering is realized in the semiconductor industry by controlled growth of one semiconductor onto another with a monolayer accuracy using atomic flat bulk crystals as the substrates. Another concept related to BCEN in the field of semiconductor is doping, which serves as the essential basis of the entire semiconductor industry. One of the goals of BCEN is to introduce such atomic level manipulation concepts into the field of colloidal nanocrystals.

Band gap engineering and doping in semiconductor science aim to tune the behavior of electrons. BCEN in solution, however, goes beyond this. For example (see the scheme in the Conspectus), BCEN structures with dual functions, such as surface catalysis and magnetic response, can be explored for developing a new generation of recyclable and high performance catalysts. Furthermore, different from band gap engineering and doping in semiconductor science, BCEN is solution-based and the resulting nanocrystals behave more like large organic/polymeric molecular species. This last feature ensures that the impact of BCEN structures shall not be limited to electronic and optoelectronic devices. Instead, they shall play a visible role in chemistry, biology, and medical sciences as well.

Industrially relevant organic compounds are dominated by “artificial molecules”, instead of “natural products”. Colloidal nanocrystals as functional materials shall likely follow the same footprints. For example, semiconductor nanocrystals are in the late stage of active research and development (R&D) and early stage of commercialization in several industrial sectors including medical diagnostics, lighting, display, and so on. Although the fundamental basis of such promises originate from size dependent properties of simple II–IV and III–V compound semiconductor nanocrystals, the nanocrystals to be incorporated in the final products will be most likely BCEN structures, such as core/shell semiconductor nanocrystals and d-dots.

3. Chemical Pathways to BCEN

Synthetic chemistry related to BCEN is still under active development. The early methods were generally poor in controlling the structure, and properties of the resulting nanocrystals were typically suboptimal. Analogous to organic chemistry, those early BCEN nanocrystals can be considered as the raw products from an organic procedure without purification. Unfortunately, nobody can figure out a general and economically feasible method to purify those early stage BCEN nanocrystals. Evidently, the most applied purification method for organic compounds, namely, chromatography, will unlikely be broadly useful for BCEN nanocrystals.

The simplest solution to the challenge of separation/purification of BCEN nanocrystals is to produce high quality products that do not require any size sorting. This actually became a general consensus in the field recently, though no written agreement exists. The confidence is largely based on the fact that, although it was a huge challenge 10−20 years ago, it is now experimentally achievable to make monodisperse and shape-controlled nanocrystals for many different compositions.

Borrowing concepts from organic synthetic chemistry, one can divide BCEN chemistry into two classes, that is, "addition BCEN" and "replacement BCEN".

3.1. Addition BCEN. Addition BCEN is to perform BCEN on an existing nanocrystal with a given structure and composition, such as a CdSe or a Fe_3O_4 nanocrystal, and each chemical step of an addition BCEN usually does not alter the structure and composition of the existing nanocrystal. In some cases, however, the alternation of the existing structure and composition is either difficult to avoid or sometimes desirable. For example, alloying during core/shell growth may yield BCEN nanocrystals with desirable properties.[9]

3.1.1. Successive Ionic Layer Adsorption and Reaction (SILAR). SILAR for colloidal nanocrystals in solution[10] is a typical "addition BCEN", which is a synthetic technique borrowed from deposition of inorganic materials onto bulk solid substrates in a monolayer-by-monolayer fashion.[11] Reports in literature confirmed that SILAR can be naturally extended to the epitaxial growth of different compositions onto one nanocrytal[12] and an excessively thick shell.[13] The main intention for introducing SILAR is to limit possible homogeneous nucleation between the cationic and anionic shell precursors by adding them separately (Figure 1, left panel).

A typical SILAR process can be illustrated using growth of CdSe/CdS core/shell nanocrystals as an example (Figure 1, left panel).[10] The presynthesized CdSe core nanocrystals were dissolved in the solvent. Upon heating the solution to the desired temperature, the cadmium precursor solution (cadmium oleate dissolved in octadecene (ODE)) and sulfur precursor solution (elemental sulfur dissolved in ODE) were added into the reaction solution in an alternating fashion. The amount of one type of precursor needed for each injection was calculated to be sufficient for the growth of one monolayer of CdS, and several minutes were needed between each injection to ensure sufficient adsorption/reaction. UV−vis, photoluminescence (PL), and transmission electron microscopy (TEM) can be used for monitoring the completion of reaction in each cycle (Figure 1). The red-shift observed in the UV−vis and PL spectra in Figure 1 (right panel) is due to the partial spreading of the exciton wave function from the core into the shell, which reflects a reduced quantum confinement because of the shell growth and can be used as a convenient probe for the epitaxial growth.[14] With the SILAR technique, monolayer and even submonolayer level accuracy is achievable.[10]

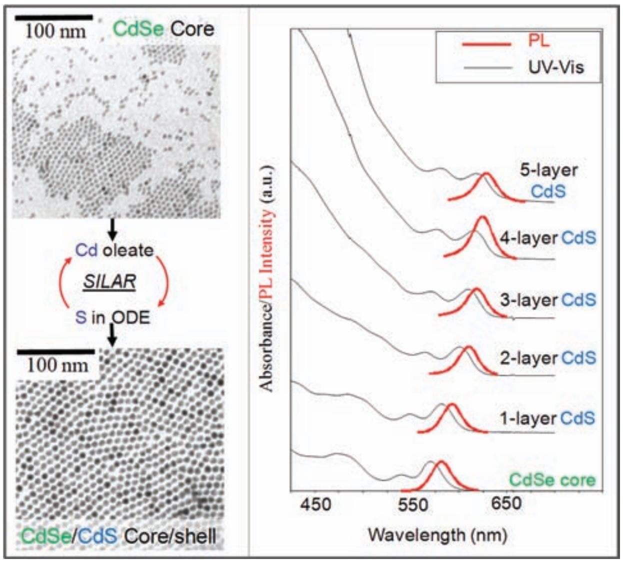

FIGURE 1. Left panel: SILAR growth of CdSe/CdS core/shell nanocrystals (five monolayers, in short as 5-layer) using nearly monodisperse CdSe nanocrystals as the cores. Right panel: Evolution of UV−vis and PL spectra of the CdSe/CdS core/shell nanocrystals in shelling.

Some variations/expansions of SILAR in solution have been reported. This includes head-on growth by SILAR,[15] one-pot SILAR,[16] and thermal-cycling-coupled SILAR (TC-SILAR),[15] The one-pot SILAR[16] method makes core/shell nanocrystals without isolating the core nanocrystals from the reaction mixture, which simplifies the operation a great deal but may complicate the control of the composition of the shell because of the residual core precursors, which is often combated by reducing the reactivity of the remaining core precursors through lowering the reaction temperature and adjusting the solution composition.[16]

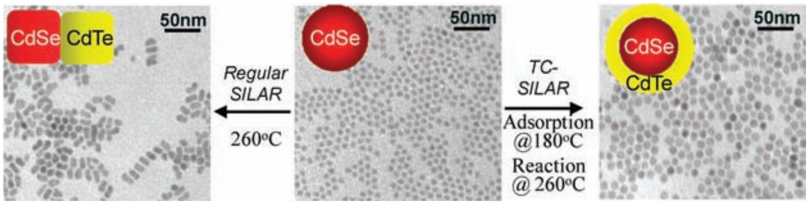

FIGURE 2. CdSe/CdTe core/shells (right) and peanuts (left) grown by TC-SILAR and regular SILAR, respectively.

If the crystal structure of core and core/shell nanocrystals has a unique axis, the SILAR process can expitaxially occur along a given direction.[15,17] In this case, by tuning the reaction temperature, the same reaction system may be tuned to produce both core/shells and peanut-shaped heterostructures (Figure 2).[15,17] Variation of reaction temperatures makes it possible to balance the adsorption and reaction. A constant high temperature shortens the absorption step, which results in nonuniform growth for peanuts (Figure 2, left). Addition of precursors at a low temperature likely allows an efficient and uniform adsorption for the spherical growth under a high reaction temperature (Figure 2, right). Except for the system shown in Figure 2, the same technique was found to be applicable for the growth of ZnSe onto spherical CdSe/CdTe core/shell nanocrystals.[17]

3.1.2. Thermal-Cycling-Coupled Single Precursor (TC-SP) Epitaxy. One molecule that contains both cationic and anionic components is called a single-source precursor, or single precursor for short. BCEN using a single precursor has a distinct advantage over that based on separated anionic and cationic precursors. Typically, because of "green chemistry" considerations,[6] available precursors for both anionic and cationic components are quite limited. For instance, fatty acid salts are the most common "greener" cationic precursors. As a result, it is sometimes difficult to choose reaction conditions for balancing the reactivity of two precursors. Furthermore, because the "greener" precursors are often not sufficiently reactive, which requires a high reaction temperature, they are thus not desirable for energy efficiency, safety, cost, and controllability. However, because of high reactivity and coexistence of both cationic and anionic components in single precursors, one should be cautious to avoid formation of nanoclusters/nanocrystals of pure shell materials. This is why the thermal-cycling-coupled single precursor (TC-SP) approach seems to be a natural path forward.[18] Similar to the case of TC-SILAR, the low temperature addition of the single precursor should help the single precursors to be uniformly distributed around each nanocrystal, instead of a local high concentration of highly reactive precursor for the formation of the pure shell material.

Figure 3a illustrates a TC-SP process that also features a single-pot approach,[18] with the precursors for formation of CdS core nanocrystals removed in situ. The single precursor ($Zn(DDTC)_2$), with its structure in Figure 3a, was added at 120 °C, and the reaction occurred at the temperature range between 160 and 200 °C, with a typical reaction temperature of 180 °C. As a control, the reaction temperature for TC-SILAR must be 220 °C to obtain the targeted core/shell nanocrystals. Although with a lower reaction temperature, the optical properties of the CdS/ZnS core/shell nanocrystals resulted from the TC-SP were substantially better than those yielded by the control TC-SILAR approach, less trap emission (Figure 3b), and higher PL quantum yield (QY) (Figure 3c). It should be pointed out that the resulting CdS/ZnS core/shell nanocrystals through TC-SP seem to be also better than the same products yielded using a similar single precursor but without thermal cycling.[19]

It was found that the reactivity of a single precursor can be tuned by the solution composition. For example, thermogravimetric analysis (TGA) measurements revealed that the decomposition of solid-state $Zn(DDTC)_2$ only started at a temperature as high as 200 °C. However, with fatty amines in the solution, this temperature dropped to about 100 °C although the growth of ZnS shell was very slow when the temperature was below about 150 °C.[18] Because both cationic and anionic components were in a single molecule, this activation shall simultaneously impact both components.

3.1.3. Controlled Doping. Doping a few ions into a nanocrystal is thermodynamically unfavorable, especially when the dopant ions do not have a matched bonding geometry with the counterions in the lattice. To meet this challenge, "decoupling doping from nucleation and/or growth" (Figure 4a) through either nucleation-doping or growth-doping was introduced for optimization of the doping process.[5] For example, the typical time scale for a "greener" synthesis of ZnSe nanocrystals is about 10 min or less,[20] but doping of Cu into ZnSe nanocrystals under similar reaction conditions could require about 2 h to complete (Figure 4b), which experimentally confirms the necessity of decoupling doping from nucleation and/or growth.

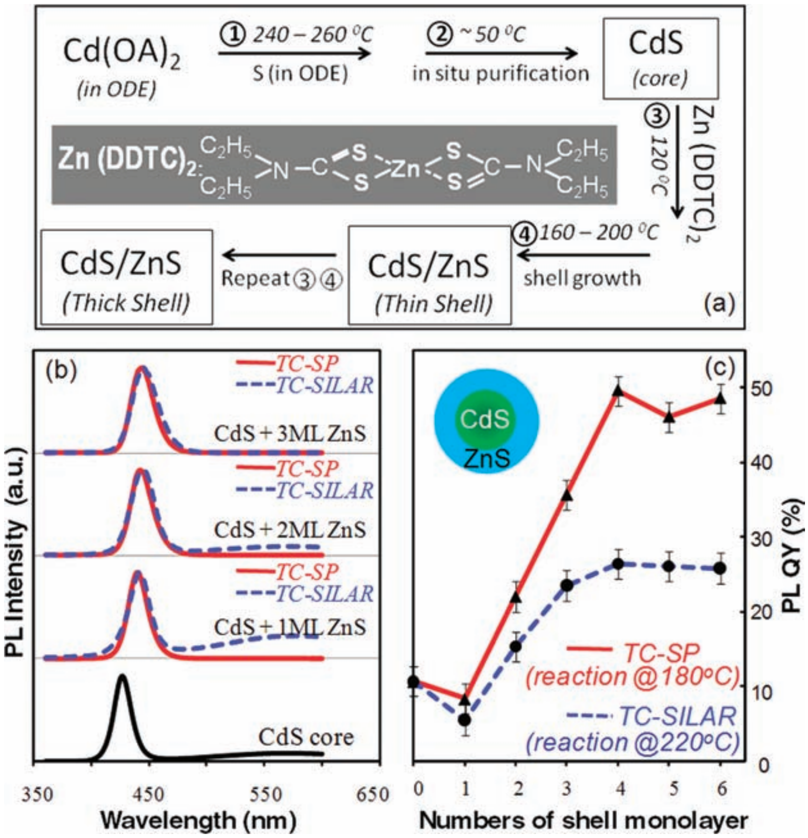

FIGURE 3. (a) Scheme of one-pot TC-SP for the growth of CdS/ZnS core/shell nanocrystals. (b,c) Comparison of the optical quality of the CdS/ZnS grown by TC-SP and TC-SILAR. The up temperatures are shown in (c), and the low temperature for both TC-SP and TC-SILAR was 120 °C.

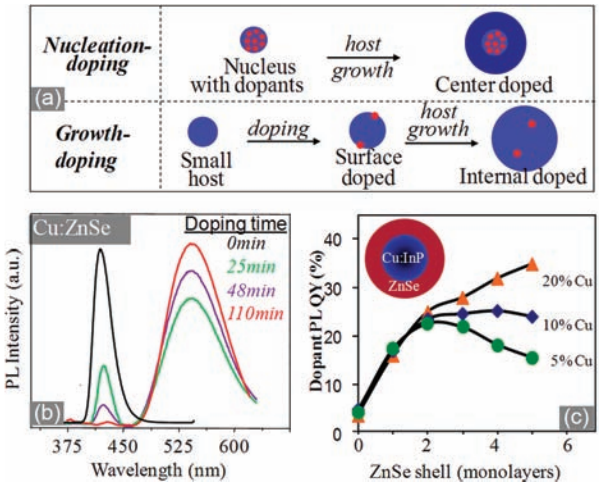

FIGURE 4. (a) Nucleation-doping and growth-doping. (b) Temporal evolution of PL spectra of ZnSe nanocrystals after the addition of Cu doping precursor. (c) Copper-doped InP (Cu:InP) with a ZnSe shell as a diffusion barrier as well as surface passivation layer.

The compatibility of dopants in the host lattice sometimes becomes very problematic, and the strategies shown in Figure 4a are not sufficient to hold the dopants within the interior of a d-dot. For example, for copper doped InP quantum dots (Cu:InP d-dots),[21] the growth-doping strategy can successfully load the copper ions onto the InP nanocrystals. However, any additional coating of pure InP onto the surface-doped d-dots (the second step for the growth-doping, Figure 4a) would remove the existing Cu dopants through "lattice-diffusion" and "lattice-ejection".[22] This is so likely because copper ions and indium ions are not isovalent. To solve this problem, ZnSe shells with different thicknesses were epitaxially grown onto the surface-doped Cu:InP d-dots. This overcoating put the dopants far away from the surface trap states, which enhanced and stabilized the dopant PL substantially (Figure 4c).[21]

3.1.4. Nonepitaxial Growth.

Epitaxial growth is mostly needed for achieving high performance optical and electronic BCEN structures. However, in some cases, nonepitaxial heterostructures are of interest as well. For example, heterogeneous catalysis using noble metal nanocrystals often requires an oxide substrate and an efficient interface, but the interface does not need to be lattice matched.

Nonexpitaxial growth often ends up with nonuniform growth of the second material onto the existing nanocrystals due to substantial strain energy. The most common resulting structures are heterodimers for dot-shaped nanocrystal seeds.[23] For nanocrystal seeds with cubic rock salt structure (PbS), growth of the second material could be limited onto certain facets to form tetrahedron or other types of metal decorations onto the PbS seeds.[24] If the starting materials are nanorods, the resulting structure could be a matchlike heterostructure, with the second material deposited onto one or two tips.[25] In the case with nanowires as starting materials, the tip effects may not be enough to localize the growth. As a result, the second material could form decorations uniformly distributed on the surface of the nanowires.[26]

Although there are quite some interesting reports along this direction, general principles are yet to be discovered. Experimental and theoretical understanding of the strain of a nanocrystal as well as the surface structure of the nanocrystal seeds shall be greatly helpful to promote this set of addition BCEN.

3.2. Replacement BCEN. Similar to the replacement reactions in organic chemistry, replacement BCEN shall replace some of the structural components of a nanocrystal. This is unique for colloidal nanocrystals as it is very difficult to run replacement reactions for an entire piece of bulk single crystal unless the temperature is excessively high and/or for a pair of very special crystal and reactants. Because of its extremely large surface to volume ratio and tiny size, however, such a replacement reaction can readily occur in a colloidal nanocrystal. Replacement BCEN is relatively new in comparison to the more straightforward addition BCEN. However, this unique chemical reaction path might impact the field of colloidal nanocrystals in both fundamental science and technical applications. For example, the interesting fast diffusion process of the ions involved in replacement reactions should shed some new light on understanding stability, doping, alloying, and growth of colloidal nanocrystals.

3.2.1. Ion Exchange BCEN. For compound nanocrystals, replacement BCEN means that one type of ion is replaced, which results in a nanocrystal with a different composition (Figure 5, top). Usually, because anions are large and form the supporting skeleton in a binary crystal, the ion exchange reactions are largely limited to cations[27] with some exceptional reports for anion exchange.[28] Amazingly, ion exchange reactions can occur rapidly and completely under very mild conditions, that is, room temperature, ambient pressure, common solvents, and regular salts as the reactants. In principle, the original cations must diffuse out of the lattice, and the new cations must take the formed vacancies rapidly to avoid the collapse of the lattice.

It is well-known that, in a bulk crystal, diffusion coefficients of ions in a ionic or covalent crystal are negligible at room temperature. Conversely, ion exchange reactions seem to be generally applicable for compound colloidal nanocrystals (at this point, reports are all based on chalcogenides). The experimental results obtained so far suggest that the exact reaction path depends on the size of the original nanocrystals.[27] For relatively small sizes (at the low end of single digit of nanometers in diameter), the reaction occurred in a concerted fashion. Conversely, the large ones took a sequential reaction, from the outside to inside. It is interesting to notice that, during ion exchange BCEN, the crystal structure may change drastically, from one type of coordination to another, from one type of cation–anion ratio to another, and from one type of lattice to another.[27,29] Again, this occurs at room temperature rapidly and completely.

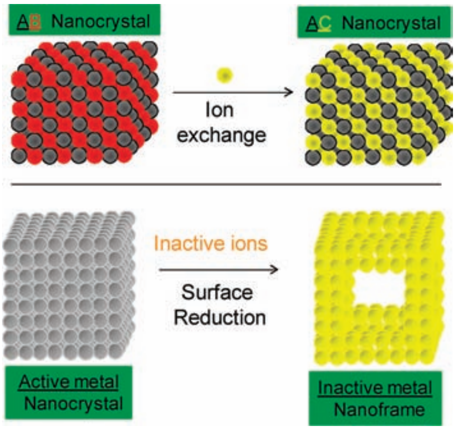

FIGURE 5. Examples of replacement BCEN: ion exchange (top) and surface reduction (bottom).

The mechanism of ion exchange reactions is mostly unknown and should be studied systematically. For example, understanding this phenomenon might help us to understand the phase-switching behavior involved in crystallization. Furthermore, this phenomenon might also play a key role in determining the quality of the resulting BCEN nanocrystals, which are often poor in surface control (reflected by their poor optical properties) and crystallinity at present.

3.2.2. Replacement BCEN Based on Redox Reactions. The most well-known example of this type is the synthesis of gold (partially alloyed with silver) nanocages and nanoframes from silver nanocubes published by the Xia's group.[30] Such a reaction relies on reduction of an inactive metal by the reductive surface electrons of the original nanocrystals (Figure 5, bottom). For example, gold ions can be reduced by silver atoms. According to electric properties of metals, the free electrons shall always be rich on the surface, especially at sharp corners and edges, of a crystal. As a result, the resulting nanostructures of the inactive metal often form an empty hole in the center of the original nanocrystals, resulting in either nanocages or nanoframes.[31] Furthermore, the final products are often alloy nanocrystals with some of the original silver atoms embedded in their interior.

A recent report pointed out that, under certain reaction conditions, reduction replacement might occur directly in a reaction system with two metal precursors.[32] In this specific report, the key was to have two different types of complexes for two metal ions involved, $[PdI_4]^{2-}$ and $[Pt(acac)_2]$. The complex $[PdI_4]^{2-}$ was more reactive under the given reaction conditions, and Pd^0 nanocrystals would thus form first. Thermodynamically, however, Pd^0 nanocrystals were not stable when there were Pt ions in the solution and surface reduction of Pt ions should occur to produce nanocages following the path shown in Figure 5 (bottom). This example reveals an interesting insight about synthetic chemistry of colloidal nanocrystals in general, in addition to its significance in replacement BCEN. While working with complex solution compositions, it is important to pay attention to the roles of each component in the solution.

The metal nanocages and nanoframes are interesting for catalysis and sensing because of their large and unique surface structure. However, it is known that metal atoms are quite mobile on the surface of nanocrystals. Consequently, intraparticle ripening could occur readily,[33] which suggests that the metal nanocages and nanoframes discussed above should be examined carefully for their stability under application conditions.

BCEN based on reactions of colloidal metal nanocrystals with oxidative anionic species, such as oxygen and sulfur, was also reported.[34] Again, the redox reactions should occur on the surface of the metal nanocrystals because of their unique electric properties mentioned above. Therefore, the resulting metal oxides and sulfides nanocrystals were hollow in the middle and usually polycrystalline.

4. Characterization of the Resulting Nanocrystals from BCEN Processes

Characterization of the complex BCEN nanocrystals is more challenging than that for common colloidal nanocrystals. If the precursors and/or nanocrystals are optically active,[35] UV−vis and PL are the most convenient probes (see Figures 1, 3, and 4 as examples), especially for semiconductor nanocrystals. TEM observations are typically useful to identify the change of size/shape of the nanocrystals. If the resulting BCEN nanocrystals have a distinguishable shape from the original nanocrystals (see Figure 2) and different components have different contrast, such as a heterodimer, TEM (especially high resolution TEM) can offer some decisive information about the BCEN. X-ray diffraction and electron diffraction can readily discriminate crystal phases if epitaxial growth verses self-nucleation is of concern, given that the new phase has different crystal lattice constants and/or crystal structure.

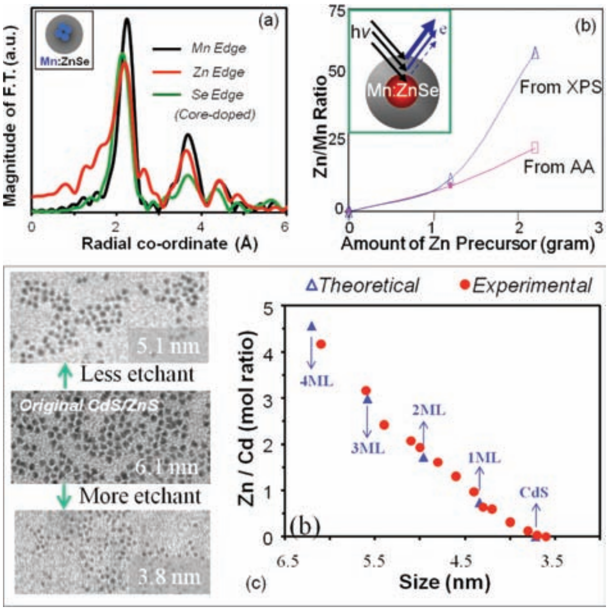

FIGURE 6. (a) XAFS spectra of core-doped Mn:ZnSe d-dots for the Mn, Zn, and Se edges. (b) Zn to Mn ratio of Mn:ZnSe d-dots (core-doped) measured using XPS and AA. Inset: scheme of XPS measurement. (c) Identification of radial distribution of elements in CdS/ZnS core/shell structure by quantitative etching. Left: TEM images of the original core/shell nanocrystals (middle), etched nanocrystals with less etchant (top), and etched nanocrystals with more etchant (bottom). Right: Zn/Cd ratio of the nanocrystals etched to different sizes; the red dots were calculated using an ideal core/shell nanocrystal model.

The central goal, also the main challenge, for characterization of BCEN nanocrystals is to identify the distribution and atomic environment of each element in nanocrystals. This is particularly difficult for those nearly spherical ones and not as problematic for those polar structures, such as heterodimers.

X-ray diffraction, electron diffraction, and high-resolution TEM can offer substantial information about the atomic environment of the majority components in a BCEN nanocrystal. For minorities, such as low concentration dopants, these techniques do not offer much help. X-ray absorption fine structure (XAFS) spectroscopy is powerful and can provide the bonding environment of a selected element. As an example, Figure 6a shows that the Mn dopant ions within a ZnSe lattice share the same lattice structure as the Zn host ions,[22c] indicating a lattice replacement doping scheme. However, the Mn ions did not have interaction with the random surface environment because the main peak at about 0.21 nm does not have the same long tail at the short distance side as that observed for the Zn XAFS spectrum (Figure 6a). Unfortunately, XAFS spectroscopy must be performed using a synchrotron facility and is not readily available to most researchers. Some spectroscopy techniques such as UV–vis, PL, and electron spin resonance spectroscopy are more accessible, but, in order to explore the atomic environment, the BCEN nanocrystals must possess specific optical activities sensitive to the local environment.[35]

The radial distribution of elements, in addition to the atomic environment of elements, is also critically important for identifying the structure and properties of the BCEN nanocrystals. X-ray photoelectron spectroscopy (XPS) has been used for quite a long time to extract such information.[14] As shown in Figure 6b (inset), XPS is a surface sensitive technique and the signal of photogenerated electrons from a given sample decreases rapidly in intensity as the depth of the sample increases.[36] Consequently, a core/shell and core-doped nanocrystal should have more photogenerated electrons from the surface components. This is why the Zn to Mn ratio measured by XPS is substantially higher than that from the corresponding atomic absorption (AA) measurements for the sample with a relatively thick pure ZnSe shell (Figure 6b). Quantitative information for a BCEN nanocrystal sample may also be obtained by computer modeling using XPS results as long as the structure is not too complicated.[14]

A quantitative etching method has been recently developed, which in principle can be applied to any type of complex nanocrystal with a nearly spherical shape.[18] Experimentally, a BCEN nanocrystal sample is etched irreversibly to a series of different sizes by controlling the amount of the etchants. The final size of each etched sample is determined by TEM (Figure 6c, left), and the corresponding elemental composition of the etched nanocrystals can be determined using different techniques, such as energy dispersive spectroscopy (EDX), atomic absorption, inductive coupled plasma-atomic emission, and so on. Plotting the composition against the size, one can obtain quantitative results about the radial distribution of elements and, by comparing with theoretical values (Figure 6c), verify the targeted structure.

5. Closing Remarks

Colloidal nanocrystals with "artificial" composition and electron band structure are expected to greatly diversify the field of nanomaterials and inorganic chemistry. Despite being promising functional materials, fundamental science associated with their synthesis, characterization, and properties is still in its infancy and deserves systematic study. Furthermore, such studies are of interest for several important fundamental phenomena, such as crystallization, surface science, and solid state chemistry.

At present, experimental evidence encourages scientists to envision a variety of complex yet elegant BCEN nanostructures as unique functional materials. With the dramatic advancement of the synthesis of high quality colloidal nanocrystals with simple composition these days, assembly techniques and the related underlying principles are going to be the most important aspects of this new synthetic field. Nature took millions of years to evolve for such complex functional structures, but we do not have such luxury. Systematic, quantitative, and cooperative efforts of scientists in the field, hopefully, will eventually bring needed functional BCEN structures into real life in a timely manner to solve the critical problem of rapid depletion of natural resources.

BIOGRAPHICAL INFORMATION

Xiaogang Peng received his B.S. (1987) and Ph.D. (1992) from Jilin University. His Ph.D. research was about Langmuir–Blodgett films with Professors Tiejin Li and Jiachong Shen. His Postdoctoral experience followed by a position as Staff Scientist at UC Berkeley with Professor Paul Alivisatos between 1994 and 1999 brought him into the field of colloidal nanocrystals. In 1999, he joined the University of Arkansas as Assistant Professor of Chemistry, and was promoted to Associate Professor in 2003 and Full Professor in 2005 (honored as Scharlau Chair Professor of Chemistry in the same year). In 2009, he joined the Department of Chemistry at Zhejiang University to start a new adventure in an old country.

FOOTNOTES

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