The production of upconverting nanostructures with tailored optical properties is of major technological interest, and rapid progress toward the realization of such production has been made in recent years. Ultimately, accurate understanding of nanostructure organization will lead to design rules for accurately tailoring optical properties. Here, the context of open questions still of general importance to the upconversion and nanocrystal communities is presented, with a particular emphasis on the structure–property relationships of core–shell upconverting nanocrystals. Although the optical properties of the latter have been thoroughly investigated, little is known regarding their atomic-scale organization. Indeed, solving the atomic-scale structure of such nanomaterials is challenging because of their intrinsic nonperiodic nature. Familiar concepts of crystallography are no longer appropriate; chemical and structural modulation waves must be introduced. To reveal the exact core–shell structures, innovative characterization techniques need to be applied and developed, as discussed herein. The continued development and application of structural characterization techniques will be vital to consolidate the currently incomplete link between atomic-scale structure and upconversion properties. This will ultimately provide a valuable contribution to the emerging detailed guidelines on how to better design upconverting nanostructures to achieve given optical properties in terms of efficiency, absorption, spectral emission, and dynamics.

1. Introduction

Although scientific research on lanthanide (Ln)-doped upconverting nanocrystals (NCs) finds its origins in the seminal works independently performed by Auzel[1] as well as Ovsyankin and Feofilov[2] in the late sixties (rooted in Bloembergen’s 1959 proposal[3] for an infrared quantum counter), research activities in this field rapidly expanded at the turn of the century. Over the last 15 years, the increased effort has led to the attainment of major milestones in the direction of nanoscale upconversion (UC) materials (Figure 1). These include the preparation of high quality Ln-doped upconverting NCs,[4] the introduction of the single- and multishell designs to improve and tune the optical properties both in terms of emission spectrum and dynamics,[5] and further improvement of UC efficiency by more exotic pathways such as crystal field engineering,[6] plasmon-enhanced upconversion,[7] dye sensitization,[8] and photonic crystal engineering.

Ln-doped upconverting NCs have risen to be one of the most-studied classes of nanoscale luminescent materials due to their fascinating optical properties associated to specific characteristics such as large anti-Stokes shift, excellent photo stability (i.e., no photobleaching), continuous emission capability (i.e., no blinking), and sharp multiline emissions. This led the UC scientific community to develop various proof-of-concept demonstrators for potential applications covering technological fields as diverse as energy harvesting,[9] anticounterfeiting,[10] barcoding,[11] super resolution nano scopy,[12] solid-state lasers,[13] as well as background-free
biological sensing and light-triggered drug delivery. Thus, in the last few years there has been an increasing effort to gain experimental control of key elementary photophysical processes associated to Ln-doped upconverting NCs, which is vital to future developments in this field. This goal is intimately linked with a better understanding of the chemical and structural organization of core–shell upconverting NCs, the subject that forms the basis for this review. Specifically, we focus on the recent progress and remaining challenges related to the comprehensive understanding of upconverting NCs atomic-scale structure.

Due to the tight focus structure of this review, many other important aspects of upconverting NCs research are not covered. However, the interested reader is referred to the many excellent reviews covering topics including basics of Ln-doped upconverting NCs, their controlled synthesis and surface functionalization, tuning of their optical properties, as well as methods to enhance UC (dye-sensitization, photonic structures), but also the emerging applications. A metareview table is provided in Figure 2 to guide the interested reader to other sources excellently dealing with these topics.

Returning to our focus on structural characterization, Ln-doped upconverting NCs are inorganic solid-state materials in which the local arrangement of atoms and forces between them control their corresponding physical properties in general and the UC properties in particular. Although, unlike semiconductor NCs, there is no effect on optical properties due to quantum confinement, the confinement of the physical dimensions in the nanoscale regime nonetheless introduces several considerations not present in bulk (i.e., microcrystalline) materials. Such effects include the lack of infinite periodicity, the high surface-to-volume ratio, and the existence of different types of interfaces.

The review is structured as follows. In the first section (Lanthanide-Doped Upconverting Nanocrystals in a Nutshell) a highly abbreviated introduction to the basics of upconversion in NCs is given to provide the minimal understanding necessary for the remainder of the review. The second section (Core–Shell Upconverting Architectures) introduces the

**Figure 1.** Lanthanide-doped upconverting nanocrystals: major milestones onto which worldwide research activities have been developing over the last 15 years. Despite that, challenges remain regarding the comprehensive understanding of associated mechanisms at the most fundamental levels. This review is going to address major challenges with a particular emphasis on the structure–property relationship. The latter is vital for the fundamental understanding of elementary photophysical processes, and thus the controlled design of innovative upconverting nanomaterials that perfectly match the needs of specific technological applications.
core-shell concepts and structures that have driven the development of the field over the last decade. In the third section (Quantitative Chemical Analysis of Core–Shell Structures), developments that recently emerged to extract information regarding the local chemical composition of Ln-doped core–shell NCs will be examined. This is followed by the fourth section (Atomic-Scale Models of Core–Shell Structures) dedicated to the limits of traditional crystallography to solve the atomic-scale structure of Ln-doped upconverting core–shell NCs. In addition, the latest developments in terms of atomic-scale structure determination applied to inorganic NCs and based on electron microscopy or total x-ray scattering are explained. Finally, the fifth section (Unconventional Upconverting Structures) reviews the emergence of interesting atypical heterogeneous architectures, reporting various examples of unconventional all-inorganic hybrid nanostructures or doping strategies that have no bulk analogues. Finally, a short outlook summarizes the review and discusses how the understanding of NC structure and its control will contribute to technological goal of upconverting NCs with a diverse range of tailorable optical properties.

2. Lanthanide-Doped Upconverting Nanocrystals in A Nutshell

Due to the excellent reviews already dealing with the photophysics underlying UC in Ln-doped upconverting NCs (see Figure 2), only a very concise overview, which is sufficient to basically understand the context of the following sections, is given here.Photon UC involving trivalent Ln ions relies on 4f-4f electronic transitions and is a nonlinear optical phenomenon that converts multiple (two or more) low energy photons into one photon of higher energy.

Figure 2. Summary of review articles published since 2009 and exclusively dedicated to lanthanide-doped upconverting nanocrystals (NCs) whose first controlled syntheses date back to early 2000s. Referenced review articles have been classified chronologically and their main focus is identified by a check mark. Note that the two reviews with an asterisk do not deal with lanthanide-doped upconverting NCs but are important for in depth introduction to upconversion and lanthanide photophysics. None of the referenced review articles deal with the structure–property relationships of lanthanide-doped upconverting NCs, which form the basis for this review.
higher energy.\textsuperscript{[15]} Such a phenomenon is typically characterized by the absorption of near infrared (NIR) radiation followed by radiative emission within the near-ultraviolet, visible, and/or NIR ranges through a number of complex pathways, reviewed, for example, by Auzel in 2004.\textsuperscript{[15b]} Also, the fundamental mechanisms of absorption, radiative and nonradiative relaxation, energy transfer, and cross relaxation that form the fundamental basis for understanding upconversion have been thoroughly covered in excellent recent reviews to which the interested reader is referred for further information on these topics.\textsuperscript{[15b,16]}

Ln-based upconverting NCs that have been developed up to now are usually designed on a common scheme that involves

---

**Figure 3.** Lanthanide-doped upconverting nanocrystals (NCs) in a nutshell: key elementary photophysical processes governing photons upconversion (top panel) and the corresponding intrinsic material characteristics (bottom panel). Distances between optically active centers as well as their corresponding local symmetry but also the phonon density of states of the host matrix all play critical roles in controlling key elementary photophysical processes. Because such intrinsic characteristics are directly linked to the underlying 3D organization of atoms, revealing the atomic-scale chemical and crystalline organizations of core–shell upconverting NCs is critical for future developments (comprehensive understanding of the structure–property relationships, design of innovative and more efficient structures etc.) in the field.
at least one sensitizer–activator pair for which the UC process relies on key photophysical steps (Figure 3, top panel), namely: i) the absorption of excitation photons by sensitizers; ii) energy migration between sensitizers until an activator is reached; iii) energy storage on the intermediate state of the activator; iv) the promotion of the activator from the intermediate level to the emitting level after a second energy migration event; and v) radiative emission from the higher energy level of the activator. All these elementary processes, in terms of efficiency or probability of occurrence, are intimately linked to intrinsic material characteristics such as distances between optically active elements and their local symmetry, or the phonon density of states (Figure 3, bottom panel), which are related to the underlying arrangement of atoms (that is, NC structure). Thus, the upconversion emission of an NC is not just related to its constituent atoms, but is intricately linked to the locations (and interactions) of the constituent atoms within the NC.

3. Core–Shell Upconverting Architectures

The core–shell concept was first introduced for Ln-doped NCs by Kömpe et al. in 2003. The authors demonstrated the realization of a core–shell architecture by growing an inert shell (LaPO₄) around an optically active core (CePO₄:Tb) for downshifting. The critical role played by the inert shell to improve the luminescence efficiency was clearly observed with an increase of the photoluminescence (PL) QY from 43% for core NCs up to 70% after the shell deposition, which was relatively close from the bulk efficiency (86%). A year later, Lehmann et al. used site-selective spectroscopy to demonstrate that the surface sites in the LaPO₄:Eu core are converted into bulk sites after growing a LaPO₄ protecting shell, Highly monodisperse downshifting core–shell NCs (NaGdF₄:Ce:Tb protected by NaYF₄) were synthesized in 2007 by Boyer et al. who observed a similar effect as reported by Kömpe and co-workers. Additionally in 2007/2008, three research groups independently reported on the significant enhancement of UC luminescence for NaYF₄:Yb:Er (KYF₄:Yb:Er) core NCs protected by a NaYF₄ (KYF₄) inert shell. Schematically this concept is shown in Figure 4A,B. The first trace of multishell upconverting NCs dates back to 2008 and was reported by Qian and Zhang for color tuning. These pioneering works performed in early 2000s established a new paradigm for the design of Ln-doped luminescent NCs and deeply reshaped the field for the next 15 years during which major concepts have emerged to tune

**Figure 4.** Energy flux management in Ln-doped upconverting nanocrystals (NCs) relies on the implementation of basic architectures. The latter have been developed over time to circumvent the limitations of pure core upconverting NCs (A) (low upconversion efficiency, difficulty to precisely tune the spectral and dynamic characteristics). Over the last decade, all developments in the field of upconverting NCs have exclusively relied on active core/inert shell (B), active core/active shell (C), and multishell structures (D). Pioneer works (red pins) at the root of these basic architectures gave rise to a wide range of structures due to the numerous combinations between sensitizer (S¹⁺, S²⁺), activator (A¹⁺, A²⁺), and migrator (M¹⁺) ions. Note that in the case of multishell architectures, the number of shells and their relative organization is used as an extra degree of freedom.
the optical properties of Ln-doped NCs, and in particular in the field of upconverting NCs. The currently known architectures to modify the efficiency, dynamics, and spectral characteristics of Ln-doped upconverting NCs are summarized in Figure 4 and can be classified either as single-shell (CS) or multishell (CSX with X ≥ 2 and representing the number of shells) structures. CS structures have been first developed and, in 2009, Vetrone et al. replaced the optically inert shell by an optically active shell (NaGdF$_4$:Yb) (Figure 4C, left panel). The role of the active shell (NaGdF$_4$:Yb) was to absorb more NIR light to subsequently transfer the energy to the activators located in the core (NaGdF$_4$:Yb:Er), leading to brighter particles compared not only to the pure core NCs but also to the inert shell counterpart. This strategy can be further extended to use the high extinction coefficient of organic dyes to increase the NCs absorption and transfer the absorbed energy into the active core (Figure 4C, right panel). In 2010, Liu et al. used an active CS structure to achieve both UC and DS in single NaGdF$_4$:Yb:Tm/NaGdF$_4$:Eu NCs. This seminal work led in 2011 to the design and synthesis of a double–shell structure (CS$_2$) to tune UC through gadolinium network-mediated energy migration for various activators with no long-lived intermediate energy levels.

Because of the known surface quenching effect with NCs, the initial work by Wang and co-workers was improved in 2012 through the growth of an optically inert shell. This is schematically shown in Figure 4D and the basic principle of controlled gadolinium network-mediated energy migration in a multishell architecture to tune the output color is given in Figure 5. The fundamental principle is based on the spatial segregation of various optically active Ln$^{3+}$ ions to control the energy flux within single NCs. In a typical scheme (Figure 5, left panel), the NIR (980 nm) pumping photons are harvested in the core region doped with the Yb$^{3+}$/Tm$^{3+}$ sensitizer–activator pair. When Gd$^{3+}$ (migrator ion) is used as the host element, the accumulated energy from the $^{1}I_6$ level of Tm$^{3+}$ can be transferred to the $^9I_{7/2}$ energy level of Gd$^{3+}$. Thus, the energy can randomly hop via the Gd$^{3+}$ atomic network and reach the first shell (Gd$^{3+}$ host element) doped with various activators, giving rise to UC luminescence. Note that the direct energy transfer between Yb$^{3+}$ and the activators located in the first shell is impossible due to the large energy transfer gaps (>7000 cm$^{-1}$). Finally, the growth of a second shell (optically inert such as NaYF$_4$) is used to maximize the UC efficiency. As can be seen in Figure 6, the UC emission can be finely tuned by using a wide range of activators such as Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$, or Dy$^{3+}$.

From 2012 up to now, the gadolinium network-mediated energy migration strategy has been reported with slight modifications mainly focused on the chemical nature of doping elements and their relative organization in multishell architectures. CSX upconverting structures have been used for multicolor emission modulated by laser power, full-color tuning through nonsteady-state UC, orthogonal excitations–emissions UC, and lifetime regulation.

It is worth noting that the gadolinium network-mediated energy migration strategy to tune the UC characteristics of CSX structures relies on a five-photon process whose efficiency as a function of the excitation power density has rarely been reported through the measurement of the corresponding absolute UCQY. As far as it is known, only recently Shin et al. have reported the absolute UCQY for LiYF$_4$:Yb/LiGdF$_4$:Yb:Tm/LiGdF$_4$:Tb:Eu/LiYF$_4$ (tetragonal phase) ranging from 1.1% to 2.5% at 106 W cm$^{-2}$.

Although CSX structures are now widely developed in the field of upconverting NCs, it is worth mentioning that significant progresses have been made with CS structures too. In 2013, Xie et al. used the active core–active shell architecture to sensitize UC luminescence with Nd$^{3+}$ ions. The latter are capable of sensitizing UC luminescence at 800 nm, which is a biocompatible
excitation wavelength that minimizes the overheating effect associated with conventional 980 nm excitation wavelength used with Yb\(^{3+}\) sensitization. The use of Nd\(^{3+}\) ions as sensitizers played a significant role in the development of dye-sensitized UC.\(^{[30]}\) The original concept relying on the use of NIR dye as an antenna for NaYF\(_4\):Yb:Er NCs was demonstrated by Zou et al. in 2012 who reported a 3300 enhancement factor for the UC luminescence despite the limited spectral overlap between the emission spectrum of the dye and the absorption spectrum of the Yb\(^{3+}\)-doped NCs.\(^{[8]}\) In 2015, Chen et al. designed an efficient active core–active shell structure sensitized by NIR dyes (Figure 7).\(^{[31]}\) The NIR-absorbing organic dyes transfer the incident energy across the organic/inorganic interface to Nd\(^{3+}\) ions located in the active shell. The energy is then transferred across the core/shell interface to Yb\(^{3+}\) ions codoped with the Tm\(^{3+}\) activators in the active core to produce luminescence via the classical energy transfer UC mechanism. This multistep cascade energy transfer strategy appears to be efficient with an UCQY of 4.8% at 15 W cm\(^{-2}\), determined by the relative method, for 50 nm CS NCs.

Regarding the UC efficiency of upconverting NCs, a significant achievement has been reported in 2018 by Homann et al. who modified the synthesis of CS β-NaYF\(_4\):Yb,Er/NaYF\(_4\) NCs to minimize the amount of residual water during the nucleation and growth steps.\(^{[32]}\) In particular, Homann and co-workers used anhydrous Ln acetates (Ln(OOCCH\(_3\))\(_3\)) as the starting precursors. The absolute UCQY as a function of
the excitation power density (up to 40 W cm\(^{-2}\)) and the luminescence decay of the Yb\(^{3+}\) emission of core and core–shell NCs with different sizes are plotted in Figure 8a,b, respectively, and compared to the microcrystalline counterpart (bulk \(\beta\)-NaYF\(_4\):Yb,Er). The absolute UCQY values vary systematically with the size and increase from 3.4% (30 W cm\(^{-2}\)) for the 15 nm core–shell NCs (inert shell \(\approx 4\) nm) to a record of \(\approx 9\)% (30 W cm\(^{-2}\)) for the 45 nm core–shell NCs (inert shell \(\approx 11\) nm). These results are of major interest because, for the first time, an absolute UCQY value very close from the one of the bulk counterpart (10.3%) is reached at the same excitation power density. According to the authors, the reduced water content in the synthesis medium due to the use of anhydrous precursors would reduce the number of hydroxy centers (known to be strong luminescence quenchers) in the crystal structure of the NCs.

The examples described in this section clearly show how past and future developments in the field of upconverting NCs are deeply rooted in energy transport management within individual NCs based on their atomic-scale organization. The importance of energy transport is also clearly presented in two recent reviews.\(^{[33]}\) Nevertheless, and despite the large number of published research articles (Figure 9, left panel) that are dedicated to Ln-doped single- and multishell upconverting NCs, the analysis of the literature also reveals that a number of fundamental questions remain unanswered (Figure 9, right panel) with regard to structural understanding, and therefore structure–property relationships. Beyond the pure fundamental interest, solving these challenging questions might ultimately lead the UC scientific community to rationally design the next generation of luminescent upconverting nanomaterials with fully tunable and predictable optical characteristics to properly fit the needs of specific technological applications in terms of efficiency, spectral emission, and dynamics. Thus, remaining core of this review will focus on the most recent breakthroughs to help in elucidating the atomic-scale organization of core–shell NCs.
the very few methods widely used to quantitatively determine the chemical composition of individual NCs. The technique is particularly well-suited in the case of single- and multishell Ln-doped upconverting NCs containing crystalline regions with compositional differences but similar crystal structures, as these cannot be distinguished from their electron or x-ray diffraction patterns. Nevertheless, it is important to keep in mind that standard chemical analyses based on EDX spectra (either maps or line scans) fail to reveal the exact local chemical organization because the electron beam propagates through regions with different compositions and the resulting quantification of EDX spectra yields to an averaged composition along the electron-beam direction (Figure 10A). In other words, the whole volume up to several tens of nanometers along the electron-beam path contributes to the detected x-ray signal. For instance, when considering the core–double shell structure (CS2) as presented in Figure 10B, the detected EDXS signal is due to various contributions of the core, inner shell, and outer shell as a function of the position of the electron beam along the scan direction x (Figure 10).

Although it is possible to determine the chemical composition of the pure outer shell at certain points (Figure 10B, zone I), as the beam scans to the middle of the NC, the detected EDX signal and derived chemical composition will be modified by the inner shell and the core (Figure 10B, zone II and zone III). In fact, average compositions of the core and shells would result from the quantification of local EDX spectra in these regions. Under such conditions, one can understand that results obtained from standard EDX analyses prevent the extraction of accurate local chemical compositions underneath the outer shell. To overcome those limitations, Kind et al.\textsuperscript{[14]} developed a procedure to extract the local composition of the core and inner shells. For this purpose, EDXS line profiles are acquired by taking EDX spectra with a strongly focused electron beam along a predefined line with the distance $\Delta x$ between two neighboring measuring positions. $\Delta x$ is chosen depending on both, the electron beam diameter $d_i$ and the particle diameter $D$. With respect to the distance between two successive measuring points, the fact that the electron beam at the bottom of the particle will be broadened to a diameter $d_f$ depending on the particle composition and size has to be considered. Beam broadening $d_f$ can be calculated according to Equation (1)\textsuperscript{[15]}

$$d_f = d_i + 0.05 \cdot \frac{Z_m}{E_0} \left( \frac{\rho}{A_m} \right)^2 \cdot D^2$$

where $Z_m$ and $A_m$ are the average atomic number and atomic mass in atomic mass unit of the particle material, $E_0$ is the energy of the electron beam in keV, $\rho$ is the particle density in g cm$^{-3}$ and $D$ is the particle diameter in nm. The minimal distance $\Delta x$ between two measuring points along the EDXS line scan must be equal or larger than $d_i$. Smaller $\Delta x$ values would result in a possible overlap of composition information from regions where successive EDX spectra are taken, which must be avoided in the compositional analysis. On the otherhand, significant compositional information may be lost for larger distances between successive measuring points, especially in the case of particles with thin shells. The choice of $d_i$ depends also on the beam current and acquisition time that is

![Figure 8. A) Upconversion quantum yield of core and core–shell particles as a function of the excitation power density. All data were derived by absolute measurements with an integrating sphere set-up. B) Luminescence decay of the Yb$^{3+}$ emission of β-NaYF$_4$:Yb,Er/NaYF$_4$ core/shell particles with a size of 15 nm (green), 22 nm (blue), and 45 nm (red). Sizes: 15 nm (green), 23 nm (blue), and 45 nm (red), open symbols stand for core particles, full symbols for core–shell particles. The reference microcrystalline upconversion β-NaYF$_4$:Yb,Er is in black. A,B) Adapted with the permission.\textsuperscript{[32]} Copyright 2018, Wiley-VCH.](image-url)
needed to obtain a statistically relevant count number in the EDX spectra and the degree of electron-beam sensitivity of the particles. For a transmission electron microscope without aberration corrector in the probe forming system, a beam diameter \(d_R = 0.8 \text{ nm}\) at the bottom of a NC with a diameter of 50 nm (assuming a composition of \(\text{Na}_{1.7}\text{Y}_{0.3}\text{Gd}_{0.3}\text{Er}_{1.7}\text{Yb}_{0.3}\text{F}_{60}\)). Note that electron beam diameter and step distances between two measuring points can be considerably smaller in transmission electron microscopes equipped with a probe corrector in the condenser system, which reduces the electron beam diameter to values significantly below 0.1 nm.

The evaluation of the composition of the shells and core of core–shell(s) NCs is performed on the basis of the following routine. First, the particle is divided into concentric subshells (SS1 to SS3) of equal thickness (Figure 10C, left panel). It is worth noting that the number and thickness of subshells are not related to the number of real shells (as initially engineered with a given chemical composition) in the particle. Subshells are only determined by the distance \(\Delta x\) between two EDXS measuring points. Second, the quantification of the stepwise recorded EDX spectra along the line scan will result in composition profiles of the chemical elements \(i\) in the NC as a function of measuring position \(x_m\), with a spatial resolution of \(\Delta x\). In the example given in Figure 10C, ten subshells are defined to map the composition of the CS2 particle. The first EDX spectrum position \(x_1\) (Figure 10C, right panel) is assumed to be taken in the middle of the first subshell at \(\Delta x/2\), the second at \(x_2 = \Delta x/2 + \Delta x\), and the 10th spectrum at \(x_{10} = \Delta x/2 + 9\Delta x\) (center of the NC). The chemical composition at each discrete position \(x_m\) is calculated without any other assumption on the chemical composition of the NC, as outlined in the following.

If \(C_i^x\) is the concentration of the chemical element \(i\) in SS1 determined by the quantification of the EDXS spectrum measured at position \(x_1\), it also represents the average concentration of element \(i\) within the first subshell such as \(C_i^x = C_{iSS}^1\). Considering that only averaged chemical compositions are obtained along the electron-beam direction, the concentration \(C_i^x\) measured at the second point \(x_2\) in SS2, is the weighted concentration of element \(i\) within the first \(\omega_1\), SS1) and second \((\omega_2\), SS2) subshells. Weights \(\omega_1\) and \(\omega_2\) are proportional to the corresponding thicknesses \(d_1\) and \(d_2\) of each subshell probed by the electron beam at point \(x_2\), respectively. Thus the concentration of element \(i\) in the second subshell \((C_{iSS}^2)\) can be calculated by using Equations (2), (3), and (4)

\[
C_{iSS}^2 = \frac{C_i^{x_1} - \omega_1 C_{iSS}^1}{\omega_2} = \frac{C_i^{x_2} - 2d_1}{2d_1 + 2d_2} C_{iSS}^1
\]

where distances \(d_1\) and \(d_2\) are only related to the particle radius \(R = D/2\) and \(\Delta x\) (see Figure 3C, right panel)

\[
d_1 = \sqrt{R^2 - (R - 1.5\cdot \Delta x)^2} - d_2
\]

\[
d_2 = \sqrt{(R - \Delta x)^2 - (R - 1.5\cdot \Delta x)^2}
\]

Similarly, it is possible to extract the concentrations of all chemical elements \(i\) at mirrored positions \(x_1', x_2', \ldots\) (Figure 10C, right panel). Then, the chemical composition of each individual subshell used to describe the NC is calculated as the average of the two corresponding mirror compositions.
(x₁, x₂, etc.) on the left-hand and right-hand sides of the center of the NC with compositional differences giving the corresponding error bars.

The technique was first applied to characterize ultrasmall (≈10 nm) single-shell upconverting NCs (Figure 11, panel A) and recently extended to large (up to 50 nm) single- and multishell structures (Figure 11B–D). These investigations shed new light on the formation of interfaces in core–shell upconverting NCs. The evidence suggested that a significant amount of intermixing between the chemical elements of the core and shell materials or between inner and outer shells materials can occur at their interfaces. This evidence for diffuse interfacial regions might not be as abrupt as previously believed. Diffuse interfaces due to the intermixing between core and shell as well as between shell and shell materials were observed not only in a size range extending from the ultrasmall regime up to 50 nm both for isotropic and anisotropic particles but also for multishell architectures and various shell growth methods (Figure 11).

These results revealing intermixing are in agreement with pioneering investigations performed in the groups of van Veggel and Haase on cation exchange reactions in trifluorides or energy exchange between Eu³⁺ and 2-naphtanoic acid. Dong and van Veggel were able to replace 92% of Gd³⁺ in GdF₃ by La³⁺ cations in just a minute at 75 °C in aqueous media.[37] Haase and Dühnen observed Förster resonance energy transfer (FRET) between Eu³⁺ and 2-naphtanoic acid located at the surface of NaEuF₄/NaGdF₄ single-shell NCs (core size: 8 nm, shell thickness: 3.5 nm).[38] Although, the degree of magnitude of the observed intermixing effect observed in our group seems to be in contradiction with the core–shell integrity proposed by Chen et al. in 2015,[39] the results can be reconciled on closer inspection. Indeed, Chen et al. reported a structure made of very large starting core NCs (NaYF₄:Ce, 40 nm) onto which a very thin shell (NaYF₄:Tb, 3 nm) was grown. The EDXS results previously mentioned showed a total rearrangement of ultrasmall (5 nm) core NCs (Figure 11, panel A) whereas only partial rearrangement was observed for much bigger (20 nm) core NCs (Figure 11, panel B). Thus, intermixing is reduced when the size of the core significantly exceeds that of the shell, bringing the aforementioned works into perfect agreement.

In addition to the size of the starting seeds and shells, other parameters were found to influence the amount of intermixing,
Figure 11. High-angle annular dark-field scanning transmission electron microscopy images of individual upconverting nanocrystals (NCs) with yellow arrows indicating EDXS scan directions and the corresponding structure-independent chemical concentration profiles for a wide variety of size, shape, shell growth methods, and architectures. (A) is dedicated to the evolution of the chemical organization of single-shell structures grown from ultrasmall isotropic NaGdF₄:Yb:Er core NCs as a function of the thickness of the shell (NaYF₄). All structures were grown by method II, which is based on the controlled hot injection of dual source precursors (NaOH and NH₄F). (B) is dedicated to the evolution of the chemical organization of single-shell (NaYF₄) structures grown from large isotropic NaEr₃Yb₂F₁₂ core NCs as a function of the shell growth methods. Methods I and III are based on the controlled hot injection of either a single source precursor (NaOOCCF₃ – method I) or sacrificial seeds (α-NaYF₄ – method III). (C) and (D) are dedicated to large double- (C) and triple- (D) shell structures grown by method I. A) Adapted with permission.[36a] Copyright 2017, American Chemical Society. B–D) Adapted with permission.[36b] Copyright 2019, Royal Society of Chemistry.
such as the shell growth methods (Figure 11, panel B). Therefore, although in specific cases the interfaces can be fairly abrupt, intermixing is a general observation in upconverting NCs, and will be important to further engineer energy transport properties. Continued efforts are still required to precisely relate structures to growth conditions and it should be noted that additional parameters not yet identified could influence the formation and characteristics of interfaces as well. Thus, the accumulation of intermixing evidence in single- and multishell upconverting NCs suggests that issue cannot be ignored and a new way of thinking is needed to properly describe the chemical organization of such complicated structures. This is also underpinned by the fact that interfacial intermixing is an important effect with different types of NCs such as quantum dots.

Interfacial intermixing plays an important role in the field of semiconductor NCs. Held et al. recently examined the radial elemental composition of core–shell nanostructures by fitting an error function model to STEM-EDX maps and applied the method to single-shell Ge/Si NCs synthesized by plasma deposition as well as to double-shell CdSe/CdS/ZnS NCs synthesized by the controlled hot-injection method (similar to the method used for single- and multishell upconverting NCs). The parameters used to extract the radial distributions of the core and shell materials were the radius of the core ($r_{\text{core}}$), the thickness of the interface ($\sigma$), the outer radius of the shell ($r_{\text{shell}}$), the roughness of the outer surface of the shell ($\sigma_s$), and finally a parameter ($p$) that describes the fraction of the residual core material in the shell, thus taking into account intermixing. The radial distributions of each element within individual NCs are reproduced here in Figure 12. These results suggest that, also in the case of semiconductor NCs, an intermixed region is formed with the core material moving out into the shell. It may be of interest to extend such modeling to allow a fraction of the shell material to also be present in the core and see whether this improves the fit to the experimental data. In any case, further EDXS experimental work and modeling is of general interest to understanding the internal chemical makeup of core–shell NCs.

Another approach, based on anomalous small angle x-ray scattering (ASAXS) to characterize interfaces in core–shell inorganic NCs has been reported by Krycka et al. for single-shell Fe$_3$O$_4$/γ-Mn$_2$O$_3$ NCs with 8.2 ± 0.2 nm average diameter (size of the starting core NCs: 6.5 ± 1.1 nm). The internal chemical boundaries of the single-shell structure were probed by ASAXS, which again revealed the existence of an intermixed region. ASAXS data modeling revealed that the final core–shell structure retained a pure Fe$_3$O$_4$ core of only 0.4 nm while a graded shell (Mn$_x$Fe$_{1-x}$)$_3$O$_4$ extended all the way to the surface of the particles. The highest content of Mn ($x=0.46$) was found in the exterior shell with a thickness of 1.7 nm, while the greatest Fe content ($x=0.4$) was observed in the inner region with a thickness of 2.0 nm. The method is particularly interesting because it is complementary to structure-independent EDXS analyses by probing ensemble-averaged chemical organization.

The formation of intermixed interfaces in multishell upconverting NCs can modify basic properties such as the chemical and structural organization of the final architecture due to the intermixed regions, which can influence the key energy transfer processes involved in UC and thereby the NCs optical properties. An important effort is needed to figure out the exact role that interfaces play in controlling both structural or chemical organizations and thus optical properties by revealing currently missing links (Figure 13). This is particularly important to increase the accuracy with which multishell systems can be designed to control emission wavelengths and lifetimes in order to allow for multiplexed detection. A number of methods described in this section indicate that an accurate description of the chemical organization of single- and multishell upconverting NCs with nanometer-scale resolution is soon within reach. However, moving even further to reveal

Figure 12. A,B) Radial (spherical) distribution of Ge and Si (A) and Cd, Zn, Se, S (B) within individual single-shell Ge/Si and double shell CdSe/CdS/ZnS nanocrystals obtained from fittings derived from an error function model. Adapted with permission. Copyright 2018, American Chemical Society.
This contains important information in terms of chemistry, cell parameters, individual atomic coordinates (i.e., atomic positions), and symmetry elements so that the repetition of such a unit cell in the 3D space (translational symmetry and space group symmetry) can be used to describe the entire crystal structure. When the infinite periodicity condition is not fulfilled or when the crystal is not perfectly periodic, as is the case for core–shell upconverting NCs (Figure 14), Bragg’s law is no longer applicable. Thus, traditional characterization techniques and algorithms developed to solve the atomic-scale structure of bulk-like materials fail to precisely determine the 3D positions of atoms. This constitutes the nanostructure problem for which a simple, one-size-fits-all solution is not on the horizon.\[42\]

In the case of core–shell upconverting NCs, a single unit cell characterized by a unique set of cell parameters \((a, b, c, \alpha, \beta, \gamma)\) is not adequate to describe the structure. The latter is by nature nonperiodic due to the segregation of different materials into concentric and nonindependent nanodomains. As schematically represented in Figure 14, core–shell upconverting NCs are better described in terms of modulation waves, which alter the unit cell of the crystal across the radius of the NC. The concept was introduced by Skrobas and Palosz to describe core NCs but is also perfectly adapted when considering core–shell structures.\[43\]

First, chemical waves can be introduced to account for a modification of the radial chemical composition of the particle from its center toward its surface depending on the relative nature between core and shell materials (Figure 14B, left panel). Second, a wave can be introduced to affect the modification of interatomic distance distributions as a function of the radial positions of atoms with respect to the center of the particle. Such a structural wave modifies \(\varepsilon(r)\), as illustrated in Figure 14B (right panel), which is a distortion parameter to quantify the relative deviation of local apparent lattice parameters \((ALPs)\) given by \(\varepsilon(r) = \frac{d - a_r}{a_r - 1}\), where \(a_r\) is a local ALP for a given radial distance, and superscripts \(C\) or \(S\) are core and shell number identifications. Note that the existence of diffuse interfaces (core/shell and shell/shell) with chemical concentration gradients as explained in Section 4 considerably modifies modulation wave profiles. The transition between two successive chemical or structural waves is not discrete (Dirac function), but rather continuous and extended. Due to the lack of periodicity in core–shell upconverting NCs, one can understand the reason why traditional crystallography and its associated computation methods either in the reciprocal or direct space fail to give a precise atomic-scale description of such challenging structures. Thus, novel approaches from crystallography are needed to precisely determine the 3D arrangement of atoms in core–shell NCs.

5. Atomic Scale Models of Core–Shell Structures

Macroscopic optical, physical, and thermodynamic properties of crystalline solids (including NCs) are linked to the underlying 3D arrangement of their atoms. Over the past 100 years, x-ray crystallography established itself as the leading technique to study the structure of matter at the atomic level. The technique is so powerful that it plays a central role in advances in many fields, including life sciences. Crystallography finds its origins in Bragg’s law of diffraction with the fundamental concept relying on the infinite periodicity of the crystal lattice. In a nutshell, the structure of crystalline materials can be described by a unit cell from just a few atoms up to several thousands of atoms per unit cell in the case of proteins.
ongoing revolution.\cite{44} Indeed, recently developed techniques are based on the precise determination of all atomic coordinates (i.e., 3D atomic positions), chemical species, and their concentrations in real materials. Although the problems related to the lack of perfect periodicity and perfect order disappear at the expense of dramatically increased complexity, such a strategy enables the 3D structure of a wide range of material to be solved. In 2017, Yang and co-workers determined the precise location of 23,000 atoms in a single 8.4 nm Fe\textsubscript{0.28}Pt\textsubscript{0.72} nanoparticle with partial chemical order (Figure 15).\cite{45} After the acquisition of a tomographic tilt series, the 3D reconstruction was computed using a generalized Fourier reconstruction algorithm. Subsequently, from the 3D reconstruction, the coordinates of all individual Fe and Pt atoms were determined by using an atom-tracing and classification method, which resulted in a 3D model with 16,577 Pt and 6,747 Fe atoms (Figure 15a).

The authors not only were able to determine the atomic positions with an average 3D precision of 22 pm, but also revealed an unknown level of complexity. The nanoparticle consists of two large L1\textsubscript{2} (chemically ordered face-centered cubic phase) FePt\textsubscript{3} grains with interlocking concave shapes. Seven smaller grains are located in between the two large L1\textsubscript{2} grains, including three L1\textsubscript{2} FePt\textsubscript{3} grains, three L1\textsubscript{0} (chemically ordered face-centered tetragonal phase) FePt grains, and a Pt-rich A1 (chemically disordered face-centered cubic phase) grain (Figure 15b). Additionally, values of the short-range order parameter clearly indicate that the central region of the nanoparticle has the highest degree of disorder and both antisite point and swap defects were observed. Finally, the authors were able to correlate the chemical order/disorder with magnetic properties by performing density functional theory (DFT) calculations of the atomic magnetic moments and magnetocrystalline anisotropy energies (MAE). The results showed that the local chemical order rather than lattice disorder is the main source that contributes to MAE.

In the field of electron microscopy, the statistical parameter estimation theory can also be implemented to solve the 3D structure of NCs.\cite{44b,44c} The aim of the theory is to precisely estimate unknown physical quantities on the basis of experimental observations. The latter are related to the quantities of interest via a known mathematical function, which is derived from physical laws and where parameters of the mathematical function represent the quantities to be determined. In the case of electron microscopy observations, simplified empirical models can be used where atomic positions and atom types are some of the model's parameters, which have to be extracted by fitting the model to the experimental electron microscopy.
images in a refinement procedure (usually called estimation procedure or estimator). In principle this approach can be used to measure compositional changes at interfaces, to count atoms with single-atom sensitivity, and to reconstruct 3D atomic structures. For instance Van Aert and co-workers combined aberration-corrected STEM, statistical parameter estimation theory, and discrete tomography to determine the atomic-scale structure of a silver nanoparticle embedded in an aluminum matrix (Figure 16A, white box). First, an empirical physics-based model was used to obtain the refined model shown in Figure 16B. Then, based on the estimated parameters, the scattered intensities were computed for each atomic column (Figure 16D). Nevertheless, the results cannot be directly interpreted in terms of the number of atoms in a column because of the broadening of the observed peaks due to a convolution of experimental noise and residual instabilities. Thus the integrated classification likelihood (ICL) criterion was evaluated (Figure 16E) to determine the number of significant peaks (ten in this case). Finally, from the estimated peak positions, the number of Ag atoms in each atomic column was quantified (Figure 16C).

The exact same procedure was applied for only two different zone-axis orientations ([101] and [100]) and the resulting atom counts presented in Figure 16C,H were used for the 3D atomic-scale reconstruction (Figure 16I). A number of atom-counting analyses were recently reported to characterize the structure of single gold nanorods and silver-coated gold nanorods,[47] probe the interface of core–shell PbSe-CdSe NCs synthesized by cation exchange reactions,[48] quantify local lattice contraction in individual CsPbBr3 NCs where Pb2+ was exchanged by several isovalent cations,[49] or determine lattice strain in gold nanorods.[50]

It is worth noting note that damage of sensitive materials (like Ln-doped upconverting NCs) by high-energy electrons poses limitations on AET but measures are available to reduce radiation damage. Knock-on damage can be reduced by performing STEM at lower electron energies. The electron beam diameter is not significantly degraded in microscopes equipped with a probe corrector if the electron energy is reduced from 200 keV or 300 keV to 80 keV and below. Damage can also be reduced by lowering the total electron dose during image acquisition. The corresponding degradation of the signal-to-noise ratio in the images can be dealt with by advanced denoising algorithms.[51] Additionally, algorithms for compressive sensing are developed, which allow recovering images from reduced data sets.[52]
5.2. Innovative Data Treatment for Total Scattering-Based Methods

Transmission-electron-microscopy-based atomic structure determination is extremely powerful and promising but the emergence of additional or complementary methods that can probe an ensemble of particles instead of just a few particles is highly desirable and in particular when considering complex modeling framework as recently introduced by Juhás and co-workers.\cite{42b} As previously explained (introduction of Section 4), traditional crystallography and its associated computation methods fail to give a precise atomic-scale description of complex nanomaterials such as core–shell NCs. In such circumstances, one can ask whether x-ray or neutron diffraction experiments are still of any interest. The short answer is yes providing that adapted methods can be used to deal with local deviations, whether as a result of significant positional disorder (due to the high surface-to-volume ratio), substitutional disorder (engineered chemical domains with interfaces), short range distortions, or anything else. The Reverse Monte Carlo (RMC) method, which was initially developed for 3D models of highly disordered systems such as liquids and amorphous structures might play a significant role to solve the atomic scale-structure of core–shell NCs in a near future. Adapted for modeling crystalline disorder,\cite{53} the basic principle of the RMC method is relatively simple.\cite{53a} A 3D configuration of atoms is modified by successive steps to minimize the difference between the calculated and experimental functions. An iterative approach is implemented in which atoms within the 3D configuration are randomly chosen and moved. After each move, the agreement between the calculated and experimental functions is tested. If the move improves the agreement, it is accepted and a new random move is proposed. Alternatively, if the proposed move worsens the agreement, a probability algorithm is used to accept the move with a reduced probability. The scheme is repeated and atoms are moved until the agreement between the calculated and experimental functions is minimized. Although the RMC method is a computer simulation approach,\cite{53b} it differs from traditional simulations because real experimental data are used to drive the development of the model instead of parameterized equations (even if constraints can be added to guide the simulation). Indeed, the typical calculated functions are the pair distribution functions (PDF) measured for real samples in a neutron and/or X-ray total scattering experiment. The RMC method was used to study structural disorder for a wide range of complex functional materials as reviewed by Playford et al.\cite{54} It is not clear yet whether the RMC method can successfully address the challenge of solving the atomic-scale structure of core–shell NCs. However, recently published results by Petkov and co-workers in this field are highly encouraging.\cite{55} The authors revealed the atomic-scale structure of pure core Pt-Pd alloyed NCs (various compositions) and extracted surface structural features that influence their corresponding catalytic properties. Realistic

Figure 16. A) Experimental HAADF STEM image of nanosized Ag clusters embedded in an Al matrix in [101] zone-axis orientation. B) Refined model of the boxed region in (A). C) Number of Ag atoms per column. D) Histogram of scattering cross-sections of the Ag columns. E) Integrated classification likelihood (ICL) criterion evaluated as a function of the number of Gaussians in a mixture model. F) Experimental HAADF STEM image in [100] zone-axis orientation. G) Refined model of the boxed region in (F). H) Number of Ag atoms per column. I) The computed 3D reconstruction of the Ag nanocluster viewed along the three different directions. A–I) Adapted with permission.\cite{46} Copyright 2011, Nature Publishing Group.
AET, atom-counting analysis, and RMC modeling are far from being routine experiments and data treatment demands a high degree of expertise to reveal the 3D structure with atomic precision. New frontiers still have to be crossed (increasing material complexity, tackling beam-sensitive materials which is the case of Ln-doped NCs), improvement of detection sensitivity, friendly software for nonspecialist etc.) but pioneering work described in this section demonstrates that overcoming the limits of traditional crystallography is possible. 3D atomic scale models of complex NCs are within reach and the case of multishell upconverting NCs is obviously challenging but not impossible. Although routinely solving the atomic-scale structure of such complex materials will not occur in the short-term, it is a worthwhile goal in order to allow true understanding of structure–property relationships, and looking to these pioneering works there are a number of things the UC scientific community can begin now to properly pave the way.

6. Unconventional Structures and Doping Strategies

The epitaxial growth concept (Figure 18) derived from thin film technology has always been considered as a good analogy to explain the formation of core–shell NCs. The two epitaxy types, namely homoepitaxy (Figure 18A) and heteroepitaxy (Figure 18B), are related to the nature of the materials. In order to tune the optical properties of core–shell NCs, very often the shell material has a relaxed lattice constant, which is different from that of the substrate (heteroepitaxy). The lattice mismatch strain \( f \) can be defined as \( f = \frac{a_s - a_c}{a_c} \) where \( a_c \) and \( a_s \) are the relaxed lattice constants of the core and the shell materials, respectively. The mismatch can take on either sign resulting in either tensile \( (f < 0) \) or compressive \( (f > 0) \) systems. Note that in the case of thin film heteroepitaxy, the absolute value of the
The increase in versatility and potential that such unconventional epitaxy opens should be exploited by the upconverting NC community. The majority of the existing literature is dedicated to core–shell systems, wherein both core and shell materials are crystallographically and chemically identical or extremely close. Such a lack of diversity is not only limiting the number of known structures, but also preventing the emergence of innovative schemes for modulating the optical properties, facilitating the post-synthesis functionalization, or improving the stability in aqueous media. In 2010, Zhang and co-workers showed that large lattice mismatches and dissimilar crystal structures between the shell and core materials did not prevent the synthesis of high-quality core–shell structures (Figure 19).\(^\text{(56)}\) Developing core–shell structures with combinations of metal, semiconducting, and upconverting-doped layers could lead to novel strategies for enhancing NC absorption, and controlling energy transfer pathways.

Regarding core–shell structures and doping strategies, just a few investigations have been reported with Ln-based NCs. In 2017, Dong et al. successfully grew \(290 \, ^\circ\mathrm{C}\) a cubic shell \((\text{CaF}_2, \, Fm\overline{3}m, \, \#225, \, a = 5.462 \, \text{Å} \, \text{relaxed}, \, \text{shell thickness} \approx 1.5 \, \text{nm})\) on top of hexagonal core NCs \((\text{NaYF}_4:Yb,\text{Er}, \, P6\overline{3}, \, \#174, \, a = 6.004 \, \text{Å}/c = 3.594 \, \text{Å} \, \text{relaxed}, \, \text{isotropic seeds with an average diameter} \approx 14 \, \text{nm})\).\(^\text{(57)}\) TEM and STEM images combined with electron and x-ray diffraction patterns are clearly in favor of the formation of a core–shell type structure (Figure 20). The authors explained that a buffer layer was formed at the interface between the hexagonal core and cubic shell to accommodate structural changes through cation substitutions between Na\(^+\) and Ca\(^{2+}\) counterbalanced by the formation of vacancies. Note that the presented data cannot be used to extract quantitative information regarding the interface. More surprising and unexpected, the authors reported an absolute UCQY of 3.7 ± 0.4% at 25 W cm\(^{-2}\) for 16.6 nm \(\beta-\text{NaGdF}_4:Yb,\text{Er}@\text{CaF}_2\) with a shell thickness of \(\approx 1.5 \, \text{nm}\). Such a large value for the UCQY is higher than the one reported by Fischer et al. (≈3% at 25 W cm\(^{-2}\)) for 24 nm \(\beta-\text{NaYF}_4:Yb,\text{Er}\) core NCs protected by a 13 nm thick \(\text{NaLuF}_4\) inert shell.\(^\text{(58)}\) The reported UCQY is also relatively close to the best UCQY reported, to date, by Homann et al. (≈5% at 30 W cm\(^{-2}\)) for 11 nm \(\text{NaYF}_4:Yb,\text{Er}\) core NCs protected by a 5.5 nm thick \(\text{NaF}\) inert shell.\(^\text{(59)}\)

As a further example of unconventional structures, in 2017, Wang et al. successfully grew \(210 \, ^\circ\mathrm{C}\) a hexagonal shell \((\text{ZnO}, \, P6_3/mc, \, \#186, \, a = 3.254 \, \text{Å} \, \text{relaxed}, \, \text{shell thickness} \approx 2.5 \, \text{nm})\) on top of hexagonal core NCs \((\text{NaYF}_4:Yb,\text{Tm}, \, P6\overline{3}, \, \#174, \, a = 5.915 \, \text{Å}/c = 3.496 \, \text{Å} \, \text{relaxed}, \, \text{isotropic seeds with an average diameter} \approx 30 \, \text{nm})\).\(^\text{(59)}\) As shown in Figure 21, experimental data suggest the formation of highly monodisperse slightly elongated core–shell type particles. No quantitative data regarding the UC properties such as lifetimes and absolute UCQY have been measured and the only comparison was made with unprotected core NCs, thus it is difficult to draw any conclusion regarding the effect (positive or negative) of the ZnO coating on the optical properties.

Equally important and complementary to the expansion of the epitaxial layers used in core–shell design are doping strategies to control and tune the optical properties of NCs. Very recently, two groups reported Ln-doped-perovskite NCs...
(CsPbX₃ with X = Cl, Br) for quantum cutting and photoluminescence (Figure 22). The idea was to combine the characteristic optical features of Ln ions with the strong ultraviolet absorption of all-inorganic perovskite NCs. Thus, the luminescence can be sensitized by energy transfer from the exciton to Ln ions. Milstein and co-workers particularly focused their investigations on Yb³⁺-doped CsPbCl₃ NCs for quantum cutting. Undoped CsPbCl₃ NCs exhibit band edge excitonic emission at 410 nm (λₑₓ = 375 nm), which is considerably reduced after Yb³⁺ doping with the emergence of intense NIR photoluminescence centered at 990 nm. Note that the average lifetime is over 2 ms, which is very close to the purely radiative limit and suggests little nonradiative quenching of the emitting excited state (⁴F₅/₂ → ⁴F₇/₂). Under optimized conditions, the authors reported a QY of 170%, which is the highest value ever measured for NCs. Additionally, photoluminescence data indicated that the sensitization is efficient even at low temperature (5 K) but also that some aspect of the sensitization is thermally assisted. Most importantly, there was no evidence of thermally activated nonradiative decay of the Yb³⁺ excited state. The origin of this efficient sensitization is attributed to extremely fast exciton depopulation due to the...
introduction of charge-compensating defects (Pb$^{2+}$ is replaced by Yb$^{3+}$) that rapidly guide (picosecond timescale) excitation energy in the vicinity of Yb$^{3+}$ activators (Figure 23).

Investigations reviewed in this section are of major interest because they clearly proved that traditional cursors such as lattice strain, symmetry, or composition, which are typically used to design core–shell structures, can be moved to completely opposite directions compared to what has been done until now. This approach can be coupled to unconventional doping strategies to discover unique photophysical properties. This yet under-investigated research area has been poorly exploited to control the optical characteristics of core–shell upconverting/downconverting structures and might reveal, in the future, interesting or unknown optical behavior.

7. Conclusions and Outlook

The crystal structure and the degree of chemical disorder in core–shell NCs are increasingly recognized to be nontrivial, and as a key to understanding their functional properties. This is of course of major interest when dealing with core–shell upconverting NCs in which the key elementary photophysical processes rely on energy transfers between optically active centers dispersed into increasingly complex and nonperiodic (although crystalline) nanostructures. The exact position of all optically active centers together with their corresponding local symmetry and relative distribution within a core–shell entity can dramatically influence energy transfer processes. As a consequence, one can easily understand that a clear picture of the underlying 3D arrangement and distribution of atoms remains of great interest both on fundamental and applied levels.

A current challenge is that core–shell upconverting NCs do not surrender details of their atomic-scale structure as readily as do their microcrystalline counterparts. Indeed, despite a century of crystallography and an impressive number of successfully solved structures, standard crystallography tools fail to reveal the exact atomic-scale organization of core–shell NCs because of their intrinsic lack of periodicity, engineered substitutional chemical disorder (interfaces), and short-range distortions. Fortunately, structural characterization methods such as AET, atom-counting analysis, and RMC modeling have recently emerged as valuable tools to tackle the nanostructure problem. Despite the complexity of these methods, they might be the
key to reveal the atomic-scale organization (both in terms of chemistry and crystal structure) of single- and multishell upconverting NCs. Although such investigations are still very scarce and have never been applied to Ln-doped upconverting NCs, they constitute innovative, promising, and highly stimulating research directions for the UC scientific community to develop a comprehensive understanding of core–shell upconverting NCs at the most fundamental level.

Additionally, there is currently no consensus in the UC scientific community on how to properly describe interfaces (sharp, diffuse, nonhomogeneous) in single- and multishell upconverting NCs. To definitely decide whether a paradigm shift is needed, a number of investigations are still needed to study the influence of: i) the shell deposition techniques, ii) the size and shape of the starting seeds, and iii) the number of shells and their relative thickness, on the final atomic-scale organization.

Figure 21. A,B) TEM images of as-prepared $\beta$-NaYF$_4$:Yb,Tm (A) and $\beta$-NaYF$_4$:Yb,Tm@ZnO (B) nanoparticles with the insets showing elemental maps (ZnO: green, NaYF$_4$:Yb,Tm: red). C) Size distributions of NaYF$_4$:Yb,Tm and NaYF$_4$:Yb,Tm@ZnO nanoparticles. D) XRD pattern (top panel) of NaYF$_4$:Yb,Tm@ZnO nanoparticles together with the standard PDF cards corresponding to $\beta$-NaYF$_4$ (middle panel) and ZnO (bottom panel). A–D) Adapted with permission.[64] Copyright 2017, Royal Society of Chemistry.

Figure 22. A) Energy level diagram of Yb$^{3+}$ ions doped in CsPbCl$_3$ perovskite nanocrystals and the possible quantum cutting mechanism. B) Energy level diagram of Eu$^{3+}$ ions doped in CsPbCl$_3$ perovskite nanocrystals and the possible photoluminescence mechanisms. A,B) Adapted with permission.[60a] Copyright 2017, American Chemical Society.
of single- and multishell upconverting NCs. It may very well be that such fundamental studies will lead to the emergence of new predictive design rules for the synthesis of upconverting nanostructures with given optical characteristics. Many of these findings may at first seem only of fundamental scientific interest, and many will probably remain within the academic realm, but some may lead to yet unforeseen discoveries and applications.

Looking into the future is of course difficult and drawing up a “to do” list for further developments in the field of Ln-doped upconverting NCs is beyond the scope of any single review. However, we venture that the continued effort to precisely determine core–shell nanocrystal structure will have an impactful future. This work in developing a more fundamental understanding of structure–property relationships will assist the ongoing progress in the modification of optical properties through structural modification of energy transport pathways. In terms of both fundamental understanding and applications, there is definitely plenty of room for developments in the field of UCNCs to continue into the next decade at their current rapid pace.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
core–shell, lanthanides, nanocrystals, structural characterization, structure–property relationships, upconversion

Received: January 25, 2019
Published online: April 3, 2019

Figure 23. A,B) Proposed La3+-induced defect emission process (A), Yb3+-sensitization mechanism involving an analogous Yb3+-induced defect state (B), and C) the proposed charge-neutral vacancy defect structure arising from doping CsPbCl3 nanocrystals with trivalent cations. A–C) Adapted with permission.[60b] Copyright 2018, American Chemical Society.

[1] F. E. Auzel, Proc. IEEE 1973, 61, 758.
[2] a) V. V. Ovsyankin, P. P. Feofilov, JETP Lett. 1966, 3, 322; b) V. V. Ovsyankin, P. P. Feofilov, JETP Lett. 1966, 4, 317.
[3] N. Bloembergen, Phys. Rev. Lett. 1959, 2, 84.
[4] H.-X. Mai, Y.-W. Zhang, R. Si, Z.-G. Yan, L.-d. Sun, L.-P. You, C.-H. Yan, J. Am. Chem. Soc. 2006, 128, 6426.
[5] a) O. Lehmann, K. Kömpe, M. Haase, J. Am. Chem. Soc. 2004, 126, 14935; b) H.-X. Mai, Y.-W. Zhang, L.-d. Sun, C.-H. Yan, J. Phys. Chem. C 2007, 111, 13721; c) J.-C. Boyer, J. Gagnon, L. A. Cuccia, J. A. Capobianco, Chem. Mater. 2007, 19, 3358; d) H. Schäfer, P. Ptaček, O. Zerzouf, M. Haase, Adv. Funct. Mater. 2008, 18, 2913; e) Q. Su, S. Han, X. Xie, H. Zhu, H. Chen, C.-K. Chen, R.-S. Liu, X. Chen, F. Wang, X. Liu, J. Am. Chem. Soc. 2012, 134, 20849; f) F. Wang, R. Deng, J. Wang, Q. Wang, Y. Han, H. Zhu, X. Chen, X. Liu, Nat. Mater. 2011, 10, 968; g) X. Li, D. Shen, J. Yang, C. Yao, R. Che, F. Zhang, D. Zhao, Chem. Mater. 2013, 25, 106; h) H. Wen, H. Zhu, X. Chen, T. F. Hung, B. Wang, G. Zhu, S. F. Yu, F. Wang, Angew. Chem., Int. Ed. 2013, 52, 13419.

[6] a) H. Dong, L.-D. Sun, Y.-F. Wang, J. Ke, R. Si, J.-W. Xiao, J. Phys. Chem. C 2015, 137, 6569; b) M. D. Wisser, M. Chea, Y. Lin, D. M. Wu, W. L. Mao, A. Salleo, J. A. Dionne, Nano Lett. 2015, 15, 1891; c) Z. Li, D. Park, G. Zborowski, J. S. Lemaire, C. J. Summers, Chem. Mater. 2014, 26, 1770; d) Q. Cheng, J. Sui, W. Cai, Nanoscale 2012, 4, 779; e) J. Wang, R. Deng, M. A. MacDonald, B. Chen, J. Yuan, F. Wang, D. Chi, T. S. Andy Hor, P. Zhang, G. Liu, Y. Han, X. Liu, Nat. Mater. 2014, 13, 157.

[7] M. Saboktakin, X. Ye, U. K. Chettiar, N. Engheta, C. B. Murray, C. R. Kagan, ACS Nano 2013, 7, 7186.
[8] W. Zou, C. Visser, J. A. Maduro, M. S. Pshenichnikov, J. C. Hummelen, Nat. Photonics 2012, 6, 560.
[9] W. Shao, G. Chen, T. Y. Ohulchansky, C. Yang, H. Agren, P. N. Prasad, Nanoscale 2017, 9, 1334.
[10] M. You, J. Zhong, Y. Hong, Z. Duan, M. Lin, F. Xu, Nanoscale 2015, 7, 4423.
[11] J. Lee, P. W. Bisso, R. L. Srinivas, J. J. Kim, A. J. Swiston, P. S. Doyle, Nat. Mater. 2014, 13, 524.
[55] V. Petkov, S. Shastri, J.-W. Kim, S. Shan, J. Luo, J. Wu, C.-J. Zhong, *Acta Crystallogr.* 2018, A74, 553.
[56] J. Zhang, Y. Tang, K. Lee, M. Ouyang, *Science* 2010, 327, 1634.
[57] H. Dong, L.-D. Sun, L.-D. Li, R. Si, R. Liu, C.-H. Yan, *J. Am. Chem. Soc.* 2017, 139, 18492.
[58] S. Fischer, N. D. Bronstein, J. K. Swabeck, E. M. Chan, A. P. Alivisatos, *Nano Lett.* 2016, 16, 7241.
[59] L. Wang, L. Ren, D. Mitchell, G. Casillas-Garcia, W. Ren, C. Ma, X. X. Xu, S. Wen, F. Wang, J. Zhou, X. Xu, W. Hao, S. X. Dou, Y. Du, *Nanoscale* 2017, 9, 18661.
[60] a) G. Pan, X. Bai, D. Yang, X. Chen, P. Jing, S. Qu, L. Zhang, D. Zhou, J. Zhu, W. Xu, B. Dong, H. Song, *Nano Lett.* 2017, 17, 8005; b) T. J. Milstein, D. M. Kroupa, D. R. Gamelin, *Nano Lett.* 2018, 18, 3792.