Core/Shell CdSe/CdS Bone-Shaped Nanocrystals with a Thick and Anisotropic Shell as Optical Emitters

Andrea Castelli, Balaji Dhanabalan, Anatolii Polovitsyn, Vincenzo Caligiuri, Francesco Di Stasio, Alice Scarpellini, Rosaria Brescia, Milan Palei, Beatriz Martín-García, Mirko Prato, Liberato Manna, Iwan Moreels, Roman Krahne,* and Milena P. Arciniegas*

1. Introduction

Colloidal nanocrystals (NCs) are highly attractive as optoelectronic materials for a wide range of applications. [1] Controlling their shape and size is paramount to tune their optoelectronic properties and to achieve high photoluminescence quantum yield (PLQY) along with narrow and tunable emission. [2] Through different synthetic strategies there is now access to a large variety of structures, from single material quantum dots, [3] nanorods, [4] and nanoplatelets (NPLs) [2a, 5] to core/shell systems that provide increased stability and photoluminescence efficiency, [6] multifunctional particles that combine metallic and semiconductor portions, [7] and highly sophisticated morphologies, such as branched [8] and hollow NCs. [9] This wealth in structural and material design translates into a broad range of applications in light emission, energy conversion, catalysis, and medicine. [1b, 10]

Core/shell nanocrystals are particularly advantageous for light emission, in particular those with a CdSe core that are epitaxially overgrown with a shell made of higher bandgap materials, such as ZnS and CdS. This is due to their efficient defect passivation, [6a, 11] the possibility to tailor the wavefunction overlap and the oscillator strength, [12] piezoelectric effects that stem from strain induced at the interface between the core and the shell, [13] and the possibility to control the self-assembly and polarization via an anisotropic nanocrystal architecture. [14] The choice of shell material allows to tailor the band alignment in the heterostructure from type I (CdSe/ZnS) [11a] to quasi type II (CdSe/CdS), [6] and fully type II (CdSe/CdTe), [15] which enables to tune the wavefunction overlap and reduce Auger recombination. [16] Auger recombination could also be significantly decreased by employing alloyed shells, [17] thick (giant) shells, [18] and gradient shell growth. [19]

Several successful strategies have been applied to fabricate anisotropic heterostructures from dot- and rod-shaped cores, leading to elongated and branched NC shapes, such as dot-in-rods, [14a, 20] rod-in-rods, [13, 20] tetrapods, [8, 21] and octapods. [22]
Concerning colloidal NPLs as cores, which represent a particularly interesting class of colloidal emitters due to their sharp emission line width and large oscillator strength, the synthesis of heterostructures with more elaborate shapes is still in its infancy. We obtain core/shell heterostructures with the NPLs as cores that are coated by a double CdS shell: a first layer, surrounding the whole NPL core, characterized by a cubic crystal structure (sphalerite-type), and an outer branched shell with a hexagonal crystal structure (wurtzite-type), composed of two tetrahedral-shaped protrusions. Despite this very complex architecture, that we name NPLs in tetrahedron dimers (NPL-i-TDs), our synthesis yields nearly monodisperse NCs whose shape resembles that of a bone. The NPL-i-TDs manifest emission in the deep red spectral region (at 660 nm) with a linewidth of around 30 nm, show a stable PLQY of 42%, and an amplified spontaneous emission (ASE) threshold of 270 µJ cm⁻². Furthermore, we observe a second emission peak at 544 nm under high pump fluence that originates from shell transitions. By combining our optical data with ultraviolet photoelectron spectroscopy (UPS) measurements, we draw a flat band diagram of these heterostructures that elucidates the origin of the red and green emission. Furthermore, the NPL-i-TDs show single mode lasing when deposited on distributed feedback (DFB) resonators with a lasing threshold below 300 µJ cm⁻², and random lasing from NPL-i-TD drop-cast films with a threshold around 50 µJ cm⁻².

2. Results

The synthesis of CdSe NPLs is well established for NCs with two to eight monolayer (ML) thickness that emit at defined wavelengths in the visible range. Additional control on the lateral size of the NPLs enables a fine tuning of the emission wavelength around these values. Here, we synthesized CdSe NPLs with 4.5 ML thickness, length of 30 ± 5 nm and width of 5 ± 1 nm, following a synthetic protocol reported by our group. More details about the NPLs are provided in Figure S1 in the Supporting Information, including representative bright-field transmission electron microscopy (BF-TEM) images and the X-ray diffraction (XRD) pattern, which shows their cubic crystal structure (sphalerite-type, see Figure S1d, Supporting Information). The 4.5 ML thickness results in a strong quantization of the electronic states along the [001] direction, and leads to a sharp photoluminescence (PL) emission peak centered at 510 nm with a full width at half maximum (FWHM) of ≈10 nm, and absorbance peaks located at 480 and 509 nm (see spectra in Figure S2, Supporting Information), in agreement with previous reports. We used these NPLs as seeds in a second reaction after a CdS shell was grown at high temperature (350 °C), following our established protocol for branched NCs with minor modifications (see the Experimental Section).

Interestingly, this synthesis approach produced monodisperse particles with an unusual anisotropic shape, as shown in the high-angle annular dark field scanning TEM (HAADF-STEM) image in Figure 1a and in the BF-TEM image in Figure S3a in the Supporting Information. The two-dimensional TEM/STEM projections of the NC shape feature a reduction in width toward the center, from ≈20 nm (p) to 10 nm (w) as shown in detail for a single NPL-i-TDs in Figure S3b in the Supporting Information, giving rise to a bone-shaped projection of the particles. The length, l, of the synthesized NCs is 30 ± 3 nm, similar to those of the initial NPLs, which can be linked to the slower shell growth along the [100]CdSe direction (Figure S3b and Table S1, Supporting Information) in the conditions used. The collected XRD patterns evidence a series of peaks that can be associated with cubic and hexagonal CdS polymorphs, while the signal of cubic CdSe seeds is not observed (Figure S3c, Supporting Information). High-resolution TEM (HRTEM) analysis confirms the presence of a cubic CdS phase in the central region (red-framed panels in Figure 1b) of the heterostructures and the hexagonal crystal structure of the CdS pods (yellow-framed panels in Figure 1b). Assuming the cubic CdS shell grows epitaxially on the CdSe NPLs, the HRTEM-deduced relative orientation of the two structures (cubic and hexagonal CdS) is compatible with the epitaxial orientation reported for the CdSe(core)/CdS(pods) octapods, i.e., CdSeCub(111)/CdS_Cub(111)/CdS_Hex(0001) and CdSeCub[2-1-1]/CdS_Cub[2-1-1]/CdS_Hex[10-10] (see details in Figure S4, Supporting Information). The presence of the CdSe NPL cores cannot be demonstrated by HRTEM, but it can be identified in HAADF-STEM imaging (see Figure 1c) due to the sensitivity of the latter technique to atomic number (Z) contrast. In these images, the higher intensity in thin stripes along the main axis of the NCs (indicated with a green arrow in Figure 1c) can be associated with the NPLs seeds, due to the presence of the Se atoms with higher Z. More images that evidence the presence of the CdSe cores in such structures are provided in Figure S5 in the Supporting Information.

The qualitative indication provided by HAADF-STEM images on the location of CdSe cores in the heterostructures is confirmed by STEM-energy-dispersive X-ray spectroscopy (EDS) mapping (Figure 1c and Figure S6, Supporting Information), which shows that Se is localized in a thin region at the center of the NCs, matching the thickness of the initial NPLs. The acquired information about the composition of the NPL-i-TDs allows to outline their growth process as follows: when the CdSe NPLs are injected in the reaction mixtures, they serve as heterogeneous nucleation points for the epitaxial growth of the CdS shell. The lack of (111) facets in the NPL discourages the direct formation of hexagonal CdS shell, and thus, at first, it promotes the formation of a cubic CdS shell. While this shell grows in thickness around the CdSe core, (111) facets might become available at the corners of the now CdSe core/cubic CdS shell structure, which provide suitable locations for the growth of a more stable hexagonal CdS shell that, in a later stage, crystallizes in pods, as it has been previously described by our group for CdSe/CdS branched NCs.

The complex geometry of the synthesized heterostructures has been derived by HAADF-STEM tomography. Few chosen projections of a selected nanoparticle and the 3D reconstructed...
The arrangement of the tips of the tetrahedra agrees with the faster growth of the hexagonal CdS shell along four of the \(<111>\) directions of the cubic CdS. In most particles, the two tetrahedra are aligned in the same direction (see Figure 2b,c), indicating the preferential growth along either the [0001] or [000-1] hexagonal CdS direction: the two directions cannot be distinguished unless a specific study of the polarity is done.\(^{[26]}\)

In the synthesis of branched core/shell NCs accurate control over the injection temperature, concentration of seeds, and the use of CdCl\(_2\) in the reaction are paramount to gain control over the particle shape.\(^{[27]}\) In the case of the NPL-i-TDs, we have found that, by varying the amount of seeds used in the reaction, we can tune the ratio of the core to shell material. A lower amount of seeds (2 nmol) leads to more developed tetrahedra still preserving the near monodispersity of the samples (Figure S7, Supporting Information). However, a drastic reduction in the seed content (0.4 nmol), while allowing to grow longer pods, yields NCs with different shapes and a noncontrolled number of pods (see Figure S8, Supporting Information). The presence of more developed tetrahedral protrusions is reflected in the XRD patterns, with a stronger intensity of the diffraction peaks associated to hexagonal CdS (Figure S9, Supporting Information). The increase in the intensity of Bragg peaks related to the hexagonal CdS phase in the XRD pattern is due to the increase in the volume of the tetrahedra when decreasing the amount of CdSe seeds in the synthesis. This is a further confirmation of the hexagonal CdS crystal structure of the tetrahedra, assessed by HRTEM, which is in agreement with other branched Cd-chalcogenides heterostructures.\(^{[8,22,28]}\)

Moreover, the volume of the CdS shell in the NPL-i-TDs is much larger than that of the core, as demonstrated by TEM analysis (see Table S2, Supporting Information). In particles synthesized by using 2 nmol of CdSe seeds, the volume of the CdSe core is 310 nm\(^3\), while that of the surrounding CdS shell with cubic lattice is roughly 1200 nm\(^3\), and the overall volume of the hexagonal lattice pods is around 1900 nm\(^3\). For a quasi-type-II heterostructure configuration, this provides a very large volume in which the electrons can be delocalized, while the holes should be confined in the CdSe core.

For the optical characterization we focus on the largest NPL-i-TDs obtained from 2 nmol seed concentration. First, we discuss their optical properties starting from the seeds. The CdSe NPLs manifest a strong quantum confinement, which leads to a bandgap of 2.45 eV (first absorption peak in Figure 3a), and in a slightly Stokes-shifted green emission at 510 nm (2.43 eV). The core/shell CdSe/CdS NPL-i-TDs show two absorbance peaks at 650 and 600 nm and a marked increase at around 500 nm (Figure 3b) that is related to absorption from the CdS shell. Here, the double peak observed in the absorption
spectrum from the CdSe cores in Figure 3a is translated to the NPL-i-TDs and therefore the two peaks in Figure 3b should also originate from transitions related to heavy and light/split-off hole levels in the CdSe core. The emission of the NPL-i-TDs is at 657 nm and therefore strongly redshifted by almost 150 nm with respect to the CdSe NPL seeds.

Such a large redshift in the emission of NPLs induced by a thick CdS shell has already been reported for core/shell NPLs\cite{24} and it was attributed to electron delocalization. Differences in the volume of the anisotropic CdS shell (however remaining in the regime with at least 1.5 nm shell thickness) lead to only minor shifts of the NPL-i-TD emission of about 2 nm (from 659 to 657 nm; the FWHM increases from 28 to 33 nm with increasing tetrahedra size; see Tables S2 and S3 and Figure S10, Supporting Information). The PLQY of the NPL-i-TDs in solution is around 42%, and this value is retained for NPL-i-TD films. The absorption and emission spectra of a film of NPL-i-TDs are reported in Figure 3c.

To assess the energy levels of the optical transitions we performed spectroscopic ellipsometry and measured the complex dielectric permittivity of the NPL-i-TD films. From the ellipsometrical parameters $\psi$ and $\Delta$, a pseudodielectric function for the NC film can be obtained and fitted with a series of damped harmonic oscillators.\cite{29} The complex dielectric permittivity can then be expressed as

$$\tilde{\varepsilon} = \sum_{j=1}^{N} \frac{\alpha_j E_{0,j}}{E^2 - E_0^2 - i\beta_j E}$$

Here $E_{0,j}$ is the central frequency (bandgap), $\beta_j$ is the FWHM, $\alpha_j$ is the oscillator strength of the $j$th oscillator describing a particular energy transition, and $E$ is the energy. We obtained good fitting with four oscillator terms and the parameters associated to the four transitions are reported in Table 1.

### Table 1. Energy ($E_0$), oscillator strength ($\alpha$), and FWHM ($\beta$) of the four peaks in Figure 3c determined by spectroscopic ellipsometry.

| Peak   | $E_0$ [eV] | $\alpha$ | $\beta$ |
|--------|------------|----------|---------|
| Peak 1 | 1.95       | 0.044    | 0.401   |
| Peak 2 | 2.10       | 0.028    | 0.221   |
| Peak 3 | 2.53       | 0.179    | 0.266   |
| Peak 4 | 2.73       | 0.326    | 0.388   |
To consolidate the association of the oscillators to the optical transitions of the NPL-i-TDs, we compared the fitted peaks in Figure 3c with the experimental absorbance spectrum in Figure 3b and found very good agreement. The emission of the NPL-i-TD films shows a single peak at low excitation fluence centered at 661 nm, which is slightly redshifted with respect to the emission from solution in Figure 3b. Interestingly, we observe a second emission peak in the green, at 544 nm (2.28 eV), from the sample with the largest CdS pods (prepared by using 2.0 nmol of CdSe seeds in the synthesis) under excitation at high pump fluence (>4.8 mW).

This behavior is analyzed in more detail in Figure 4, where the emission spectra at different values of the pump power are plotted. The (red) PL peak at 1.88 eV first increases approximately linearly with pump power, and then its intensity saturates around 4 mW. At approximately the same pump power the second (green) peak, at 2.28 eV, appears and gains quickly in intensity. Consequently, the NPL-i-TDs film manifests dual emission with well separated emission peaks in the red and green part of the visible spectrum at excitation power higher than 4.8 mW.

We could obtain further insight into the band structure of the core/shell NPL-i-TDs through UPS.[10b] Figure 5a shows the full UPS spectrum versus the binding energy, where the Fermi level is set at 0 eV.

The low binding energy onset of 1.7 eV (Figure 5b) corresponds to the difference between the Fermi level and the top of valence band, while the signal onset at the high binding energy (low kinetic energy) side (Figure 5c) yields the energy difference from the Fermi level to the vacuum level. Combining these values with the information from the optical transitions (hexagonal CdS bandgap of 2.53 eV, emission at 1.88 and 2.28 eV) we sketch the band alignment of the core/shell heterostructure as depicted in Figure 5d. Here we assigned the low binding energy offset to the hexagonal CdS valence band. Furthermore, we assumed a quasi type-II charge distribution for the CdSe/CdS system, as reported in literature for CdSe cores with strong confinement.[30] We did not consider alloying at the CdSe/CdS interface, as STEM and Raman analysis (Figures S5 and S11, Supporting Information, respectively), suggest that, if present, it would be minimal. For the cubic and hexagonal structure of CdS, we considered a conduction band offset of ≈115 meV and valence band offset of ≈50 meV,[31] which could in the NPL-i-TDs slightly deviate due to strain or confinement effects.[32] Therefore, the bandgap of the hexagonal CdS shell is slightly larger and is shifted upward in energy with respect to the cubic one. The green emission that we observe from the NPL-i-TDs is at lower energy than that, for example, reported from

Figure 4. PL spectra of a drop-cast film of NPL-i-TDs excited with femtosecond pulsed laser at 400 nm at different excitation power. The inset shows the PL amplitude as a function of the excitation power for the peaks at 1.88 eV (red) and 2.28 eV (green).

Figure 5. a–c) Ultraviolet photoelectron spectrum recorded from the NPL-i-TDs sample that allows to identify the valence band and Fermi level energies with respect to vacuum. d) Flat band diagram of the NPL-i-TDs with CdSe core, and cubic and hexagonal CdS shell. The numbers give the energy differences in eV and the dashed ellipses indicate the two emitting channels of the NPL-i-TDs.
CdSe/CdS dot-in-rods and tetrapods at high pump fluency\(^{[33]}\). Considering the band diagram in Figure 5d, it is plausible that this lower emission energy in the NPL-i-TDs results from the type-II offset between the cubic and hexagonal CdS phase. Such radiative recombination of the excitons in the shell at higher pump fluence occurs when the core recombination channel is saturated, which is corroborated by the fluence threshold for the observation of the green emission. Furthermore, we only observe the dual emission from the NPL-i-TD sample with the thickest shell (2 nmol seed concentration).

**Figure 6a** shows the emission spectra of a drop-cast NPL-i-TDs film under femtosecond pulsed excitation (\(\lambda = 400\) nm) and increasing pump fluence. We observe an ASE band at the high-energy side of the PL peak, which indicates repulsive exciton interactions\(^{[34]}\). The ASE threshold is 270 \(\mu\)J cm\(^{-2}\), which is significantly higher than what is obtained on CdSe core-only\(^{[35]}\) and on CdSe/CdS NPLs with a thin shell,\(^{[5c]}\) but within one order of magnitude comparable to other CdSe/CdS core/shell structures.\(^{[18a,23b,33a,34]}\) While the complex shell morphology of the NPLs-i-TDs is not optimal for ASE and lasing, these structures provide a peculiar exciton delocalization, and therefore, they can be very appealing for applications where electron and hole states should be localized in different portions of the nanocrystal volume.

The FWHM of the ASE peak increases with increasing excitation fluence, with the peak broadening occurring on the high energy side of the spectrum. To test the lasing capabilities of our samples, we chose DFB resonators as a cavity since these are technologically highly appealing for solution processable materials. Here, the lasing device can be simply fabricated by drop casting the emitter solution on a silica substrate into which a suitable grating was etched, thus filling the structure with NCs. For a DFB the cavity mode is determined by the Bragg-Snell law\(^{[46]}\)

\[
m \lambda = 2d \sqrt{n_{\text{eff}}^2 - \sin^2 \Theta}
\]

where \(d\) is the grating periodicity, \(n_{\text{eff}}\) is the effective refractive index of the emitting film, \(m\) is an integer, and \(\Theta\) is the angle under which the emission is detected. We obtained lasing with a grating periodicity \(d = 350\) nm under a detection angle of 5° with respect to the surface normal. Combining these parameters and setting \(m = 2\) yields to an effective refractive index of \(n_{\text{eff}} = 1.83\). This value is in excellent agreement with the one that we obtained by ellipsometry from NPL-i-TD films (\(n_{\text{eff}} = 1.86\)).

Interestingly, drop-cast films of NPL-i-TDs on planar glass substrates also show random lasing, as demonstrated in Figure 6c and Figure S12 in the Supporting Information. Here a set of sharp peaks (with \(0.5\) nm FWHM) in emission is observed that fluctuate with time, as evident in the two consecutive spectra for two different pump fluences reported in Figure 6c (in red and black, respectively). The statistical appearance of the lasing peaks is a characteristic feature of random lasing, as for example evident for the peak labeled “A” that only appears in the second spectrum recorded at higher fluence.

**3. Conclusions**

We showed that the seeded-growth protocol for fabricating branched nanocrystals, such as CdSe/CdS octapods, can be applied to highly anisotropic seeds, in particular to CdSe nanoplatelets with only few monolayers thickness. The resulting nanocrystals maintain the CdSe nanoplatelet core, and the overall length of the platelets, but manifest a double CdS shell composed of an inner part with cubic crystal structure and an outer one, made of two tetrahedra with hexagonal crystal structure. The shell increases in thickness toward the short edges of the nanoplatelets, forming overall bone-shaped nanocrystals. The thick shell leads to an excellent stabilization of the optical properties in thin films and results in a type-II band alignment that favors shell-related transitions at high excitation fluence. The bone-shape CdSe/CdS core/shell heterostructures show high and stable PLQY for red emission from the band edge, and dual emission in the red and green spectral region under increased pump fluence, as well as ASE and lasing from thin...
films. Overcoating such structures with an additional ZnS shell could be a promising strategy to further increase their luminous efficiency. The design of complex shell morphologies that consist of different lattice geometries, and which manifest gradients in thickness, opens new perspectives for core/shell heterostructure materials. Different shell thickness morphologies could be employed to control the multie exciton distribution in such heterostructures and could lead to dipole moments that depend on the exciton population and excitation fluence.

4. Experimental Section

Materials: Cadmium chloride (CdCl₂, 99.99%) and octadecylphosphonic acid (ODPA, 97%) were purchased from Sigma-Aldrich; cadmium oxide powder (CdO, 99.999%), sulfur powder (S, 99%), tri-n-octylphosphine oxide (TOPO, 99%), and tri-n-octylphosphine (TOP, 97%) were purchased from Strem Chemicals; hexylphosphonic acid (HPA) was purchased from Polycarbon Industries. All chemicals were used as received and all the syntheses were carried out using a standard Schlenk line.

Synthesis of CdSe/CdS NPL-i-TDs NCs: CdSe NPLs were synthesized according to a previously published procedure.[5f] In a three-neck flask CdO (60 mg), CdCl₂ (6 mg), TOPO (3 g), ODPA (290 mg), and HPA (80 mg) were degassed for 1 h at 140 °C under stirring. The solution was heated up to 350 °C under N₂ flow. When the solution became transparent (~270 °C), anhydrous TOP (2.5 mL) was injected in the flask. Once the temperature reached 350 °C, the CdSe seeds (in hexane), TOP (500 µL), and S precursor (620 µL of the 32 mg mL⁻¹ solution in TOP) were quickly injected. The reaction was run for 10 min before quickly cooling it down to room temperature. When the temperature was below 100 °C, anhydrous toluene (3 mL) was added to the resulting product. The particles were then washed twice via a solvent/antisolvent protocol with an anhydrous mixture of ethanol and methanol and dispersed in toluene. The size and shape of the NPL-i-TDs were tuned using different amounts of CdSe seeds that were synthesized following a reported protocol.[5j]

Structural, Optical, and Surface Characterization: BF-TEM analyses were carried out on a JEOL JEM-1011 (JEOL, Tokyo, Japan) microscope, operated at 100 kV acceleration voltage, and equipped with a tungsten thermionic electron source. HAADF-STEM images and tilted series were carried out on a JEM-1011 (JEOL, Tokyo, Japan) microscope, equipped with a tungsten thermionic electron source. HAADF-STEM images and tilted series were carried out on a JEM-1011 (JEOL, Tokyo, Japan) microscope, equipped with a tungsten thermionic electron source.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
Keywords
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