Near-Infrared Photoluminescence Enhancement in Ge/CdS and Ge/ZnS Core/Shell Nanocrystals: Utilizing IV/II—VI Semiconductor Epitaxy

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ABSTRACT Ge nanocrystals have a large Bohr radius and a small, size-tunable band gap that may engender direct character via strain or doping. Colloidal Ge nanocrystals are particularly interesting in the development of near-infrared materials for applications in bioimaging, telecommunications and energy conversion. Epitaxial growth of a passivating shell is a common strategy employed in the synthesis of highly luminescent II—VI, III—V and IV—VI semiconductor quantum dots. Here, we use relatively unexplored IV/II—VI epitaxy as a way to enhance the photoluminescence and improve the optical stability of colloidal Ge nanocrystals. Selected on the basis of their relatively small lattice mismatch compared with crystalline Ge, we explore the growth of epitaxial CdS and ZnS shells using the successive ion layer adsorption and reaction method. Powder X-ray diffraction and electron microscopy techniques, including energy dispersive X-ray spectroscopy and selected area electron diffraction, clearly show the controllable growth of as many as 20 epitaxial monolayers of CdS atop Ge cores. In contrast, Ge etching and/or replacement by ZnS result in relatively small Ge/ZnS nanocrystals. The presence of an epitaxial II—VI shell greatly enhances the near-infrared photoluminescence and improves the photoluminescence stability of Ge. Ge/II—VI nanocrystals are reproducibly 1—3 orders of magnitude brighter than the brightest Ge cores. Ge/4.9CdS core/shells show the highest photoluminescence quantum yield and longest radiative recombination lifetime. Thiol ligand exchange easily results in near-infrared active, water-soluble Ge/II—VI nanocrystals. We expect this synthetic IV/II—VI epitaxial approach will lead to further studies into the optoelectronic behavior and practical applications of Si and Ge-based nanomaterials.

KEYWORDS: germanium · core/shell nanocrystals · IV/II—VI epitaxy · near-IR photoluminescence · quantum dots

ARTICLE
Some Ge syntheses reportedly produce fluorescent (photoluminescent) Ge nanocrystals. Reduction of GeCl₄ with NaBH₄ in polyvinylpyrrolidone (PVP) at room temperature (rt)¹⁸ and laser ablation of H-terminated Ge wafers¹⁹ produce violet (380 nm) and blue (450 nm) emitting Ge nanocrystals, respectively. Templated oxidative polymerization of Zintl (Ge₉)₄ clusters produces hexagonal Ge mesopores (3.1 – 3.2 nm pore size) characterized by large surface areas (404–451 m²/g) and tunable (1.3 – 2.2 nm), wall thickness-dependent photoluminescence (PL, 640 nm) tunable (1.3).²⁶ Although near-IR PL (exceptions are uncommon among optical materials)⁴¹,⁴² as an example, the small lattice mismatch (–3.7%, Table 1) between isostructural CdSe and CdS allowed the growth of thick epitaxial CdS shells on top of CdSe cores.⁴⁳–⁴⁵

The resulting high quality, “giant” CdSe/CdS core/shell nanocrystals remain the best example of nonblinking quantum dot fluorophores to date,⁶⁶–⁵² which allowed their use in 3D superlocalization, dynamic tracking, and subdiffraction spatial resolution luminescence depletion imaging.⁵³–⁵⁵ In contrast, the large lattice mismatch (–11%, Table 1) between CdSe and ZnS did not allow the growth of real (complete) ZnS shells on CdSe cores. Only isolated ZnS islands could be grown on the surface of CdSe cores.⁶⁶ For this reason, we decided to investigate shell materials that can adopt a cubic, zinc blende structure with a similar lattice parameter to that of cubic, diamond Ge. Several II–VI and III–V semiconductors are available for this purpose (Table 1). However, we focused on II–VI semiconductors because these are known to be much more chemically and photochemically robust compared to III–V semiconductors. Here, we specifically explore CdS and ZnS as shell materials because the lattice mismatch between these and Ge is relatively small at +3.1 and –4.4, respectively (Table 1). In addition, the valence and conduction energy levels of Ge, CdS and ZnS are such that either type I (Ge/ZnS, Ge/CdS) or quasi-type II (Ge/CdS) heterostructures could be possible depending on the relative size of the Ge core and the thickness of the II–VI shell (Figure 2).⁶⁷

**RESULTS AND DISCUSSION**

**Ge Crystal Chemistry.** Elemental germanium adopts the diamond crystal structure that is common to all group IV semiconductors (C, Si, Ge, Sn, Pb) (Figure 1). This diamond structure is topologically similar to, or isotopic with the zinc blende (spinelite) crystal structure adopted by many II–VI and III–V semiconductors. In both the diamond and zinc blende structures, each and every atom (or ion) is tetrahedrally coordinated. In the diamond structure, the same atom occupies all positions (for example, Ge as in Ge–Ge–Ge–Ge) (Figure 1a), whereas in the zinc blende structure, two different ions alternate positions (for example, Zn²⁺ and S²⁻ as in Zn–S–Zn–S) (Figure 1b).

**Selecting Shell Materials for Ge Epitaxy.** Because highly crystalline semiconductors tend to possess superior optical qualities, core/shell and multilayer nanostructures require the structure of their individual components to be similar enough so that all interfacial boundaries remain defect-free. In other words, interfacial epitaxy between the different phases must have strict continuity. In a core/shell, this can only be accomplished when the core and shell materials have identical and/or very similar crystal structures or, more specifically, when both materials are isotypical and share a similar lattice constant.

**IV/II – VI Epitaxy: Synthesis of Ge/CdS Core/Shell Nanocrystals.** Nanocrystalline Ge cores, freshly synthesized by reduction of Gel₂ with n-butyllithium,³² were reacted with enough Cd and S precursors alternately to form one atomic monolayer (ML) of CdS at a time using the successive ion layer adsorption and reaction (SILAR) method.⁴⁴,⁵⁷ We originally carried out this procedure...
maximum band gap widening due to the cubic CdSe are also shown for comparison. The reported for Ge, ZnS and CdS semiconductors. Si, ZnSe and are considered.

Figure 2. Compilation of valence and conduction energy levels, as well as ionization potentials and electron affinities reported for Ge, ZnS and CdS semiconductors. Si, ZnSe and CdSe are also shown for comparison. The “QD” levels represent maximum band gap widening due to the effect of quantum confinement in low dimensional (nanosized) semiconductors.

<table>
<thead>
<tr>
<th>core/shell</th>
<th>crystal structure</th>
<th>lattice parameters, Å (% lattice mismatch)</th>
<th>band gap type</th>
<th>bulk value, eV (nm)</th>
<th>core quantized (qdot) range, eV (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV/IV and II–VI core/shells</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>diamond</td>
<td>5.658 (0)</td>
<td>indirect</td>
<td>0.664 (1870)</td>
<td>1.46 – 0.77 (850 – 1600)</td>
</tr>
<tr>
<td>Si</td>
<td>diamond</td>
<td>5.431 (–4.0)</td>
<td>indirect</td>
<td>1.12 (1110)</td>
<td>–</td>
</tr>
<tr>
<td>CdS</td>
<td>zinc blende</td>
<td>5.832 (+3.1)</td>
<td>direct</td>
<td>2.40 (520)</td>
<td>–</td>
</tr>
<tr>
<td>ZnS</td>
<td>zinc blende</td>
<td>5.4063 (–4.4)</td>
<td>direct</td>
<td>3.60 (344)</td>
<td>–</td>
</tr>
<tr>
<td>ZnSe</td>
<td>zinc blende</td>
<td>5.6676 (+0.17)</td>
<td>direct</td>
<td>2.70 (460)</td>
<td>–</td>
</tr>
<tr>
<td>II–VI/III–V core/shells (previously synthesized)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CdSe</td>
<td>wurtzite</td>
<td>4.299, 7.010 (0)</td>
<td>direct</td>
<td>1.74 (713)</td>
<td>2.53 – 1.94 (490 – 640)</td>
</tr>
<tr>
<td>CdS</td>
<td>wurtzite</td>
<td>4.1348, 6.749 (–3.7)</td>
<td>direct</td>
<td>2.40 (520)</td>
<td>–</td>
</tr>
<tr>
<td>ZnS</td>
<td>wurtzite</td>
<td>3.814, 6.258 (–11)</td>
<td>direct</td>
<td>3.60 (344)</td>
<td>–</td>
</tr>
<tr>
<td>III–V/II–VI core/shells (previously synthesized)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>InP</td>
<td>zinc blende</td>
<td>5.860875 (0)</td>
<td>direct</td>
<td>1.34 (925)</td>
<td>2.53 – 1.77 (490 – 700)</td>
</tr>
<tr>
<td>CdS</td>
<td>zinc blende</td>
<td>5.832 (–0.63)</td>
<td>direct</td>
<td>2.40 (520)</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 1. Structural and Optical Properties of II–VI and IV Semiconductors: Cores vs Possible Epitaxial Shell Materials

*Calculated lattice mismatches for II–VI/III–V and II–VI/II–VI core/shells are similar regardless of whether zinc blende (cubic) or wurtzite (hexagonal) structures are considered. InP/CdS were reported to have a wurtzite structure. Calculated as 100[(shell lattice parameter – core lattice parameter)/core parameter]; positive (+) and negative (–) values correspond to core-to-shell lattice expansion and compression, respectively.

addition does not matter. Starting with Cd precursor addition, followed by S addition (Cd first, S second) was just as effective in growing thick CdS shells atop Ge cores.

Figure 3 shows transmission electron microscopy (TEM) analyses for a typical shell growth procedure. Starting with cubic Ge cores (with a size or diameter of 4.6 ± 0.7 nm), we were able to grow Ge/nCdS with varying shell thicknesses of up to ca. n = 20 CdS monolayers (MLs); Ge/3.1CdS (6.4 ± 0.8 nm), Ge/4.9CdS (7.4 ± 1.0 nm), Ge/10.5CdS (10.7 ± 1.3 nm), and Ge/18.8CdS (15.5 ± 1.8 nm) (Table 2). All the Ge/CdS core/shell nanocrystal samples have a narrow size distribution (11 – 13%), comparable or narrower than the initial Ge cores (15%); thus, their isolation did not require any size selection.

During CdS shell growth, the shape of the Ge/CdS core/shells slowly transforms from spheres (Ge and Ge/3.1CdS) to tetrahedral prisms (Ge/10.5CdS and Ge/18.8CdS) (Figure 3a–d). A tetrahedral morphology is usually a strong indication of a cubic crystal structure. However, powder X-ray diffraction (XRD) (Figure 4) and selected area electron diffraction (SAED) (Figure 3f) are both consistent with all the Ge/CdS core/shells containing a mixture of hexagonal and cubic structures. We believe a plausible explanation for the observed shape evolution is that the original cubic (diamond) structure of the Ge cores could be dictating the final shape of the Ge/CdS core/shells. Crystalline Ge is a covalent material made up of strong Ge–Ge bonds. Cubic to hexagonal transformations of Ge may thus involve a large activation energy barrier and may not be nearly as common as for II–VI semiconductors. In fact, hexagonal Ge remains unknown under standard ambient conditions. In contrast, the epitaxial CdS shell could easily adopt a hexagonal (wurtzite) structure, or a cubic (zinc blende) structure, or any combination of the two. On the basis of the XRD data, Ge/nCdS core/shells...
having between 5 and 19 MLs are anywhere between 7 and 17% cubic and between 83 and 93% hexagonal (see Methods). This is consistent with the fraction of the core/shells made up by the relatively small Ge core. On the basis of the number of MLs calculated from TEM data (size histograms), the theoretical Ge core volume falls quickly from 23 to 3% on going from Ge/4.9CdS to Ge/18.8CdS, respectively (Table 2). We also note that, among the possible impurities for Ge-based materials, neither the initial Ge cores nor the resulting Ge/CdS core/shells showed any conclusive evidence of GeO2, GeS2 or GeS (Figure 4).

Elemental mapping and composition analyses of several individual particles by energy dispersive X-ray spectroscopy (EDX) confirmed the presence and homogeneous distribution of all three Ge, Cd and S elements within all particles. These data, summarized in Table 2, show good agreement with the theoretical elemental composition calculated from the number of MLs obtained from TEM. Figure 5 shows representative EDX elemental mapping data for Ge/10.5CdS core/shell nanocrystals. Because the core makes only a very small fraction of the sample (ca. 8% in volume, see Table 2), the Ge signal-to-noise (S/N) ratio is low. Nevertheless, we found no evidence of phase segregation in any Ge/II-VI sample using EDX.

**Synthesis of Ge/ZnS Nanocrystals.** We explored a similar SILAR procedure to grow epitaxial ZnS shells on Ge cores. This resulted in Ge/ZnS nanocrystals (3.8 ± 0.7 nm) that are of comparable size or even slightly smaller than the initial Ge cores (4.6 ± 0.7 nm) (see Figure S1, Supporting Information, and Table 2). EDX data of several such particles across multiple areas of different samples consistently showed the presence of all three Ge, Zn and S in significant ratios: 13 ± 3, 37 ± 5 and 49 ± 5 atom %, respectively (Table 2). Of course, it is impossible for the particle size to decrease upon shell growth. Thus, the original Ge cores must be undergoing either etching and/or partial exchange by ZnS.33,34,58 Because the resulting nanocrystals still show the NIR photoluminescence characteristic of Ge, these nanocrystals must have either a core/shell or graded Ge/ZnS composition.62 Why this etching or exchange occurs with ZnS and not with CdS is presently unknown, but there are some clues: On the basis of lattice parameters, ZnS leads to compression (−4.4%) while CdS leads to expansion (+3.1%) of the Ge core (Table 1). In addition, according to Pearson’s theory of hard and soft acids and bases (HSAB),63,64 Zn2+ is a borderline acid while Cd2+ is a soft acid. Also, the 0.1 M Zn(oleate)2 precursor solution contains a somewhat higher concentration of excess oleic acid (0.68 M) compared to the 0.1 M Cd(oleate)2 precursor.
TABLE 2. Synthesis of Ge/II–VI Core/Shell Nanocrystals

<table>
<thead>
<tr>
<th>composition: Ge, M (Cd or Zn), S</th>
<th>theoretical Ge core volume (nm)</th>
<th>XRD phase(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample</td>
<td>size (nm)</td>
<td>theoretical EDS</td>
</tr>
<tr>
<td>Ge</td>
<td>4.6 ± 0.7</td>
<td>100, 0, 0</td>
</tr>
<tr>
<td>Ge/3.1CdS</td>
<td>6.4 ± 0.8</td>
<td>40, 30, 30</td>
</tr>
<tr>
<td>Ge/4.9CdS</td>
<td>7.4 ± 1.0</td>
<td>25, 38, 38</td>
</tr>
<tr>
<td>Ge/10.5CdS</td>
<td>10.7 ± 1.3</td>
<td>9, 46, 46</td>
</tr>
<tr>
<td>Ge/18.8CdS</td>
<td>15.5 ± 1.8</td>
<td>3, 49, 49</td>
</tr>
<tr>
<td>Ge/ZnS</td>
<td>3.8 ± 0.7</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

a Theoretical Ge and II–VI volumes were calculated using the Ge core and II–VI shell sizes (diameters and thicknesses, respectively) measured by TEM. b Partial Ge etching may have occurred (see Supporting Information); exact no. of MLs unknown. c Not determined.

Figure 4. Powder X-ray diffraction patterns of Ge, Ge/CdS and Ge/ZnS nanocrystals (experimental), and of bulk GeO2, Ge, CdS and ZnS (for comparison).

Figure 5. EDX elemental mapping of Ge/10.5CdS nanocrystals does not show any clear evidence of phase segregation (Notes: Shown are four identical or “registered” areas within the same sample; only 8% of this sample’s volume is made of Ge, see Table 2).

Figure 6. Representative solution phase absorption spectra (a) and solid phase (film) absorption spectra (calculated from diffuse reflectance data (b) for Ge/CdS core/shell nanocrystals. The two clear absorption edges evident at 520 nm (a) and ca. 800 nm (b) originate from the thick CdS shell29,30,44,45 and Ge core,46–50 respectively.

TABLE 3. Representative Photoluminescence Properties of Ge/II–VI Core/shell Nanocrystals

<table>
<thead>
<tr>
<th>sample</th>
<th>QY (%)</th>
<th>PL enhancement</th>
<th>Lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>0.0004</td>
<td>× 104</td>
<td>n.d.</td>
</tr>
<tr>
<td>Ge/3.1CdS</td>
<td>0.050</td>
<td>× 120</td>
<td>2280 ± 30</td>
</tr>
<tr>
<td>Ge/4.9CdS</td>
<td>1.2</td>
<td>× 2930</td>
<td>2740 ± 11</td>
</tr>
<tr>
<td>Ge/4.9CdS in water</td>
<td>0.0029</td>
<td>× 7</td>
<td>596 ± 52</td>
</tr>
<tr>
<td>Ge/10.5CdS</td>
<td>0.066</td>
<td>× 160</td>
<td>2440 ± 32</td>
</tr>
<tr>
<td>Ge/18.8CdS</td>
<td>0.0060</td>
<td>× 15</td>
<td>1820 ± 261</td>
</tr>
<tr>
<td>Ge/ZnS</td>
<td>0.23</td>
<td>× 560</td>
<td>551 ± 13</td>
</tr>
<tr>
<td>Ge/ZnS in water</td>
<td>0.0072</td>
<td>× 18</td>
<td>943 ± 19</td>
</tr>
</tbody>
</table>

a Typical error in QY determination is 15% of the indicated value (see Methods). b Relative PL intensity of the brightest Ge cores was arbitrarily set to 1. c Not determined: PL was too weak to accurately measure a lifetime.
solution (0.24 M) (see Methods). Successful growth of thicker epitaxial ZnS shells on Ge cores will require further optimization of reaction conditions, and will be the subject of a separate article in the future.

**Photoluminescence Enhancement in Ge/II–VI Nanocrystals.**

Growth of an epitaxial II–VI shell greatly enhances the NIR PL intensity and improves the NIR PL stability of Ge nanocrystals (Table 3, Figures 6 and 7). All the Ge/CdS core/shells and Ge/ZnS nanocrystals we have made showed NIR PL and retained their NIR PL over a period of several months, regardless of shell thickness or composition. Among the Ge/CdS core/shell nanocrystals with different number of MLs that we studied, Ge/4.9CdS had the highest NIR PL quantum yield of 1.2% (almost three thousand times brighter than the best Ge cores), as well as the longest PL decay lifetime of 2.74 \( \pm 0.01 \) \( \mu \)s (Table 3 and Figure 7). Additional shell growth lowered the relative PL intensity, as observed previously for giant, thick-shelled CdSe/CdS core/shell nanocrystals (an effect that was attributed to the eventual appearance of cracks or defects due to increasingly large strain effects).\(^{29,44,45}\) Nevertheless, all Ge/II–VI nanocrystals consistently showed one-to-three (10–1000 \( \times \)) orders of magnitude more intense NIR PL compared to the brightest bare Ge nanocrystals that we ever obtained, which produced only 0.0004% QY (if and when emission was detectable). In fact, Ge cores made by reduction of GeI\(_2\) with nBuLi in hexadecylamine and ODE (see Methods) were only photo luminescent in a minority of cases; roughly one out of every 10 or 20 Ge batches made produced measurable PL. Because even the best Ge cores were very weakly emitting, we were unable to measure their PL lifetime (Figure 7b). While the lack of a Ge core-only excited-state lifetime prevents a definitive statement, we note that measured core/shell lifetimes, as shown in Figure 7 and summarized in Table 3 (single exponential fit of the long-lived decay), all fall within a factor of 5 of each other for various CdS shell thicknesses as well as for ZnS. Such comparable lifetimes suggest Type-I band alignment as suggested in Figure 2 for these compositions.

To confirm that Ge, rather than CdS traps, are responsible for the observed near-IR PL (900–1100 nm), we recollected the photoluminescence data utilizing a redder excitation. As shown in Figure 8, the PL spectra of Ge/CdS core/shell nanocrystals collected using 532 nm vs 705 nm laser excitation are very comparable. Because the CdS shell, with a band gap of ca. 520 nm (2.48 eV), cannot absorb or get excited with the much redder 705 nm laser, we conclude that the Ge core, rather than the CdS shell, is indeed responsible for the observed near-IR emission.

**Aqueous Solubilization via Ligand Exchange.** Ge/II–VI nanocrystals easily transfer from organic (typically toluene, hexane or chloroform) to aqueous phase upon ligand exchange with a suitable, water-soluble thiol. Scheme 2 graphically shows this procedure using Ge/4.9CdS and mercaptosuccinic acid as a representative example (see Methods) (Figure 9). Unfortunately,
ligand exchange and/or water solubilization results in a decrease of PL intensity. However, the resulting watersoluble Ge/II–VI nanocrystals are still ten times ($10\times$) brighter than the best, uncoated Ge cores (Table 3), which cannot be easily transferred to water.

**CONCLUSIONS**

Inspired by the prospect of using IV/II–VI epitaxy in colloidal semiconductors, we carried out a thorough investigation on the colloidal synthesis of thick-shelled Ge/MS (M = Cd or Zn) core/shell nanocrystals. We chose CdS and ZnS as shell materials based on their low lattice mismatch with crystalline Ge. Freshly prepared Ge cores were alternately reacted with enough metal (Cd or Zn) and sulfur (S) precursors to form one epitaxial atomic monolayer at a time using the SILAR method. Elemental mapping confirmed the presence and homogeneous distribution of Ge, M (Cd or Zn) and S elements in all samples. Further, we did not find any evidence of phase segregation in the several Ge/CdS and Ge/ZnS nanocrystals that we made and measured.

In addition, analysis of Ge/CdS core/shells with different shell thickness showed a strong correlation between their theoretically expected and experimentally measured elemental compositions. We observed the shape evolution (morphology transformation) of Ge/CdS nanocrystals from spheres to tetrahedral prisms during shell growth. We believe the original cubic structure of the Ge cores played an important role in dictating the final morphology of the Ge/CdS core/shells. In contrast to Ge/CdS, Ge/ZnS nanocrystals did not show the expected larger particle size compared to the initial Ge cores. We tentatively attribute this behavior to combined etching and exchange effects of the specific Zn and/or S precursors used here on the original Ge nanocrystalline cores.

Growth of a II/VI (CdS or ZnS) shell greatly enhances the near-infrared (NIR) photoluminescence intensity and improves the NIR photoluminescence stability of Ge nanocrystals. In general, all Ge/II–VI heterostructures showed 1–3 orders of magnitude more intense NIR emission compared to the original Ge cores. All the Ge/II–VI nanocrystals retained their NIR photoluminescence after several months. Ge/4.9CdS showed the highest NIR quantum yield and longest PL lifetime. Although there is clearly room for improvement, the achieved PL level is already three thousand times brighter than the most emissive Ge cores we were able to make using literature procedures. Additional CdS shell growth caused a decrease in quantum yield, possibly because of the introduction of defects due to strain effects. Ge/II–VI nanocrystals easily transfer from organic to aqueous phase upon thiol ligand exchange. We expect that these results will extend the arsenal of quantum dot fluorophores available, particularly near-IR active quantum dots, for fundamental optoelectronic studies as well as for biological imaging and tracking, telecommunications, and energy conversion applications.

**METHODS**

**Materials.** Cadmium oxide (CdO, 99.99%), zinc oxide (ZnO, 99.99%), sulfur (3%, 99.99%) and oleic acid (90%) were purchased from Alfa Aesar; n-butyllithium (n-BuLi, 1.6 M hexane solution), dioctylamine (octyl2NH, 98%), tetramethylammoniumhydroxide pentahydrate (Me4NOH·5H2O, 97%) and mercaptosuccinic acid (97%) from Sigma-Aldrich; hexadecylamine: (octyl)2NH (12.5 mL, 41.36 mmol) was degassed under a vacuum at 80°C until optically clear. 0.1 M Cd(oleate)2-amine: (octyl)2NH (12.5 mL, 41.36 mmol) was degassed under a vacuum at 80°C for 20 min. 0.2 M Zn(oleate)2-amine: (octyl)2NH (12.5 mL, 41.36 mmol) was degassed under a vacuum at 80°C for 30 min, refilled with air, and transferred to another flask containing 0.2 M Cd(oleate)2.0.2 M Cd(oleate)2: CdO (318 mg, 2.48 mmol), oleic acid (3.09 g, 10.94 mmol), and ODE (7.11 g, 28.16 mmol) were degassed under a vacuum at 80°C for 60 min, refilled with Ar, and heated to 240°C until optically clear. 0.1 M Cd(oleate)2-ammine: (octyl)2NH (12.5 mL, 41.36 mmol) was degassed under a vacuum at 80°C for 30 min, refilled with Ar, and heated to 240°C for 30 min.

**Synthesis.** Ge Cores. Ge was synthesized by a modified literature procedure.26 Inside a dry N2-filled glovebox, Ge2 (0.05 g, 0.15 mmol), hexadecylamine (0.75 g, 3.11 mmol) and a Teflon-coated stir bar were added to an oven dry, four-neck 250 mL round-bottom (RB) flask. The flask was fitted with a condenser, and the system was sealed and brought out and connected to a vacuum line. The contents were degassed under a vacuum at 80°C for 30 min, refilled with dry Ar, and heated to 200°C. After 5 min at this temperature, a mixture of n-BuLi (0.2 mL of 1.6 M hexane solution) and ODE (0.75 mL) made inside the dry-N2 filled glovebox was quickly injected. The mixture was heated to and annealed at 300°C for 1 h. The mixture was then allowed to cool down to rt. The freshly prepared Ge cores were allowed to remain in the crude solution (without washing) under a constant stream of dry Ar until further processing (see shell growth below).

Ge/MS Nanocrystals (M = Cd or Zn). Precursor solutions: Cd, Zn and S stock solutions were made by a previously reported procedure.44 0.2 M Cd(oleate)2: CdO (318 mg, 2.48 mmol), oleic acid (3.09 g, 10.94 mmol), and ODE (7.11 g, 28.16 mmol) were degassed under a vacuum at 80°C for 60 min, refilled with Ar, and heated to 240°C until optically clear. 0.1 M Cd(oleate)2-ammine: (octyl)2NH (12.5 mL, 41.36 mmol) was degassed under a vacuum at 80°C for 30 min, refilled with Ar, and transferred to another flask containing 0.2 M Cd(oleate)2. The mixture was stirred at 60°C for 20 min. 0.2 M Zn(oleate)2: ZnO (203 mg, 2.49 mmol), oleic acid (6.18 g, 21.88 mmol), and ODE (4.41 g, 17.47 mmol) were degassed under a vacuum at 80°C for 60 min, refilled with Ar, and heated to 240°C until optically clear. 0.1 M Zn(oleate)2-ammine: (octyl)2NH (12.5 mL, 41.36 mmol) was degassed under a vacuum at 80°C for 30 min, refilled with Ar,
and transferred to another flask containing 0.2 M Zn(oleate)₂
(12.5 mL). The mixture was stirred at 60 °C for 20 min. 0.1 M S₈
precursor solution: S₈ (790 mg, 2.47 mmol) and ODE (19.73 g, 78.13 mmol) were degassed under a vacuum at 80 °C for 30 min, re- 
illled with Ar, and heated to 180 °C for 20 min until optically clear. 

Shell growth: ODE (1.5 mL, 4.69 mmol) and diocylamine (1.5 mL, 4.96 mmol) were introduced to the four-neck 250 mL 

R8 flask containing freshly made Ge cores. The mixture was degassed under vacuum at 80 °C for 30 min, refilled with Ar, and heated to a constant shell growth temperature 230 °C. 

M (Cd or Zn) and S precursors were introduced in an alternating fashion using two programmable syringe pumps, each followed by a 15 min wait period. Either the S (preferred) precursor or the 

M precursor (Cd or Zn, also okay) was injected first. Shell growth was monitored by absorption or transmission electron micro-

scopy (TEM) (below) using aliquots (0.05 mL) taken at different shell growth stages. The mixture was allowed to cool to rt

15 minutes after the last M (Cd or Zn) or S injection. Purification: 

Core/shell nanocrystals were washed three times by precipita-

tion with 1:1 or 1:3 v/v acetone/methanol mixtures and cen-

trifugation at 4200 rpm for 5 min, using each time toluene as the

redissolution solvent. Transfer to water via ligand exchange: 0.5 mL of “crude” (unpurified) Ge/Ms and mercaptosuccinic acid (100 mg, 0.67 mmol) were dissolved in toluene (2.5 mL). A solution of tetramethylammonium hydroxide pentahydrate (600 mg, 3.31 mmol) deionized water (3 mL) was added. The mixture was transferred into a vial coated with aluminum foil and nitrogen, water-soluble Ge/Ms were washed once or twice by precipitation with brine (saturated 

NaCl solution) and centrifugation at 4200 rpm for 5 min, using each time deionized water as redissolution solvent.

**Structural Characterization.** Powder X-ray diffraction (XRD) was measured using Cu Kα radiation on a Rigaku Ultima U4 dif-

fractometer. Quantitative estimates of relative phase abund-

ces (% cubic vs % hexagonal) of Ge/II–VI nanocrystals were performed using Rietveld analysis on PowderCell 2.3. 

Transmission electron microscopy (TEM) was conducted on carbon-coated copper grids using FEI Tecnai G2 F20 field emission transmission electron microscope (STEM) at 200 kV (point-to-point resolution <0.25 nm, line-to-line resolu-

tion <0.10 nm). Elemental composition was characterized by energy-dispersive X-ray spectroscopy (EDS). For particle analysis, dimen-
sions were measured manually or with ImageJ for >200 particles. Average sizes (diameters) are reported ± standard deviations.

**Optical Characterization.** Absorption spectra were measured with an Agilent 8453 UV–vis photodiode array spectrophot-

ometer. Steady-state PL spectra were measured by exciting the sample with a 532 nm diode laser and directing the collected PL to an avalanche photodiode.

**Conflict of Interest:** The authors declare no competing financial interest.

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**Supporting Information Available:** TEM and particle size data for Ge/ZnS nanocrystals. This material is available free of charge via the Internet at http://pubs.acs.org.

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