Communication

Cd$_3$P$_2$/Zn$_3$P$_2$ Core-Shell Nanocrystals: Synthesis and Optical Properties

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1. Introduction

The size, surface, and composition-dependent optical properties of semiconductor nanocrystals (NCs) give them great potential in range of biomedical (imaging, sensing) and optoelectronic (LEDs, solar cells) applications [1–5]. As synthesized, the optical properties of semiconductor NCs are typically sensitive to ambient conditions (air, moisture), so to truly exploit them in next-generation biomedical and optoelectronic applications, surface passivation reactions are required [1]. The formation of a core-shell semiconductor NC is the most common surface passivation reaction, involving the growth of another material, usually a semiconductor over the NC core. The optical properties of a core-shell NC are highly tunable by considering the electronic properties of the core and shell materials [6–8]. For example, by changing the band alignments of the core and shell, a whole host of optical properties can be altered including absorbance and emission maximum, quantum yield, blinking rates, and an increased resistance to oxidation can be gained [9–12]. There are countless examples of systems, II–VI, IV–VI, and III–V-based nanomaterials where the optical properties have been transformed and exploited thanks to the development of robust core-shell syntheses [10,13,14].

The II–V semiconductor nanocrystals such as Cd$_3$P$_2$ and Zn$_3$P$_2$ have enormous potential as materials in next-generation optoelectronic devices requiring active optical properties across the visible and infrared range. To date, this potential has been unfulfilled due to their inherent instability with respect to air and moisture. Core-shell system Cd$_3$P$_2$/Zn$_3$P$_2$ is synthesized and studied from structural (morphology, crystallinity, shell diameter), chemical (composition of core, shell, and ligand sphere), and optical perspectives (absorbance, emission-steady state and time resolved, quantum yield, and air stability). The improvements achieved by coating with Zn$_3$P$_2$ are likely due to its identical crystal structure to Cd$_3$P$_2$ (tetragonal), highlighting the key role crystallographic concerns play in creating cutting edge core-shell NCs.

Abstract: II–V semiconductor nanocrystals such as Cd$_3$P$_2$ and Zn$_3$P$_2$ have enormous potential as materials in next-generation optoelectronic devices requiring active optical properties across the visible and infrared range. To date, this potential has been unfulfilled due to their inherent instability with respect to air and moisture. Core-shell system Cd$_3$P$_2$/Zn$_3$P$_2$ is synthesized and studied from structural (morphology, crystallinity, shell diameter), chemical (composition of core, shell, and ligand sphere), and optical perspectives (absorbance, emission-steady state and time resolved, quantum yield, and air stability). The improvements achieved by coating with Zn$_3$P$_2$ are likely due to its identical crystal structure to Cd$_3$P$_2$ (tetragonal), highlighting the key role crystallographic concerns play in creating cutting edge core-shell NCs.

Keywords: nanomaterials; quantum dots; nanocrystal; core-shell nanostructure; cadmium phosphide; zinc phosphide; synthesis; shelling
detection applications. Surface passivation reactions for II–V are underdeveloped compared to the conventional II–VI and IV–VI materials with only a handful of successful reports [20–22]. Cd$_3$P$_2$ absorbs light on a large wavelengths scale with emission across the visible and NIR range (450–1500 nm) with quantum yields of up to 70%, and consequently is an ideal material for light energy conversion, optoelectronic, and telecommunication applications [23–27]. With robust formation protocols [26–30], Cd$_3$P$_2$ NCs appear as a perfect model to take up the challenges associated to this family and in particular that of growing a shell. Indeed, one of the biggest challenges in utilizing the II–V semiconductors is their extreme sensitivity to air and moisture. To the best of our knowledge, only two examples of coating have been reported for Cd$_3$P$_2$. Our group synthesized Cd$_3$P$_2$/ZnS core-shell NCs which showed stable emission 6 weeks post air exposure [26]. However, the shell was thin (0.3 nm), leading to batch dependent air stability. Ding et al. [31] reported the encapsulation of Cd$_3$P$_2$ NCs within silica nanobeads and polystyrene microspheres. Multiple QDs are contained within the microspheres making their practicality problematic [31]. These strategies having their limits, moving forward there is a great opportunity to study shelling methods for II–V semiconductor nanocrystals.

The purpose of this paper is to investigate the shelling of Cd$_3$P$_2$ nanocrystals with Zn$_3$P$_2$ which is an alternate material exhibiting tetragonal structure (this system could be seen as the analog of CdSe/ZnS). The synthesis and optical properties of core/shell Cd$_3$P$_2$/Zn$_3$P$_2$ NCs are comprehensively examined from chemical, structural, and optical perspectives. In contrast to the cubic ZnS material previously used, Zn$_3$P$_2$ leads to a robust type I heterostructure and opens new avenues of fundamental study and Cd$_3$P$_2$ based applications.

2. Materials and Methods

2.1. General Synthetic Considerations

All synthetic modifications were carried out in either an argon-filled glovebox with O$_2$ and H$_2$O levels below 0.1 ppm or an argon-filled Schlenk line with a vacuum level between 100 and 150 mTorr. All used glassware was dried in an oven ($115^\circ$C) overnight before use. Solvents used, mesitylene, toluene, and pentane, were collected from a puresolv solvent system and degassed with argon for at least 1 h before loading them into the glovebox. Oleylamine was degassed with argon and dried over 4 Å molecular sieves before use.

2.2. Synthesis and Purification of Cd$_3$P$_2$ Cores Stabilized with Hexadecylamine

*In situ synthesis of Cd(OAc)$_2$(HDA)$_2$: In an argon-filled glovebox 0.1728 g (0.75 mmol) of anhydrous cadmium (II) acetate (99% STREM, Newburyport, MA, USA) is added to a 50 mL Schlenk tube along with either 0.4221 g (1.75 mmol) of hexadecylamine (HDA) (98% Sigma Aldrich, St. Louis, MO, USA). Next, 4 mL of anhydrous toluene (99.9% Honeywell, Charlotte, NC, USA) is added to Schlenk tube, which is then sealed via septa (mixture appears cloudy). The Schlenk tube is then brought out of the glovebox and hooked up to a Schlenk line. The rubber tube connecting the Schlenk tube to the Schlenk line then undergoes 3 cycles of evacuation and purging with argon, before opening the Schlenk tube to the line. The Schlenk tube is then plunged into an oil bath set to 40 $^\circ$C. The mixture is left to react for 3 h, to insure precursor formation.

*Synthesis of Cd$_3$P$_2$ NCs: In an argon-filled glovebox, 0.0671 g (0.25 mmol) of tris(trimethylsilyl) phosphine (98% STREM) is weighed out and dispersed in 1 mL of toluene. **CAUTION:** tris(trimethylsilyl) phosphine is pyrophoric, producing toxic byproducts upon exposure to air and moisture. Tris(trimethylsilyl) phosphine is then withdrawn into a 3 mL syringe and brought out of the glovebox. The syringe containing tris(trimethylsilyl) phosphine is then inserted into the Schlenk tube containing Cd(OAc)$_2$(HDA)$_2$ and is swiftly injected. Immediately upon injection, a color change is observed from cloudy white (Cd(OAc)$_2$(HDA)$_2$) to yellow. Over the next 5 min, several more color changes are observed, going from yellow to orange, then red, and finally dark
red. After 2–3 h, the color resembles a dark velvet green. The reaction is then left to react overnight (18 h).

**Purification of Cd$_3$P$_2$ cores stabilized with hexadecylamine:** Unpurified Cd$_3$P$_2$ cores are then transferred into a glovebox and added to a 25 mL Nalgene centrifuge tube (Thermo Fisher) that contains a gas tight rubber O-ring (ensuring an argon atmosphere is maintained during centrifugation). Anhydrous acetonitrile (99.8% Sigma Aldrich) is then added to the unpurified Cd$_3$P$_2$ cores in a 3:1 ratio (i.e., 12 mL of acetonitrile to 4 mL of Cd$_3$P$_2$ cores). The centrifuge tube is then spun at 25,000 RPM for 25 min. After centrifugation, the centrifuge tube is re-entered into the glovebox and the supernatant (light yellow color) is decanted. The centrifuge tube containing Cd$_3$P$_2$ as a pellet is then dried under vacuum on a Schlenk line to remove traces of toluene and acetonitrile. Washed Cd$_3$P$_2$ cores are then dispersed in 5 mL of oleylamine (98% primary amine Sigma Aldrich).

### 2.3. Synthesis and Purification of Cd$_3$P$_2$/Zn$_3$P$_2$ Core-Shell Nanocrystals

**Synthesis of Cd$_3$P$_2$/Zn$_3$P$_2$:** 2 mL (0.054 mmol) of purified Cd$_3$P$_2$ cores stabilized with hexadecylamine is added to a 50 mL RB flask. The RB flask is then brought out of the glove box and connected to a Schlenk line. After 3 cycles of evacuation and purging with argon, the RB flask is opened to the line. A temperature probe is then put through one of the RB flasks septa and the reaction heated to 160 °C (ramp rate 25 °C per minute). When the reaction reaches 160 °C, 0.112 g (0.324 mmol) of zinc (II) tris(N,N’-diisopropylacetamidinato) dispersed in 1 mL of oleylamine is added dropwise over a one minute period. After 2 min, 0.0054 g (0.216 mmol) of tris(trimethylsilyl) phosphine (98% STREM) dispersed in 1 mL of oleylamine is added dropwise to the RB flask over a one-minute period. The reaction mixture is then heated to 180 °C and left for 2 h.

**Purification of Cd$_3$P$_2$/Zn$_3$P$_2$:** Cd$_3$P$_2$/Zn$_3$P$_2$ synthesized at low and high temperature is purified in an identical fashion to Cd$_3$P$_2$ cores. The only difference is the purification cycles are repeated twice more with Cd$_3$P$_2$/Zn$_3$P$_2$, i.e., giving a total of 3 purification cycles. Post purification Cd$_3$P$_2$/Zn$_3$P$_2$ are dispersed in toluene.

### 2.4. Sample Characterization

Low- and high-resolution TEM analysis is performed at the “Centre De Microcaractérisation Raimond Castaing” on a JEOL JEM 1400 electron microscope operating at 120 kV with a point resolution of 4.5 Å and for HRTEM analysis on a JEOL 2100F operating at 200kV with a point resolution of 2.5 Å. Additional high resolution TEM is performed in a Hitachi HF3300 microscope equipped with a Cs corrector. STEM-EDS is performed in a Phillips CM20FEG equipped with a Brüker SDD detector. Samples for TEM analysis are prepared in glovebox by slow evaporation of a drop of the colloidal solution deposited onto a carbon-covered copper grid. The size distributions are determined by measuring at least 250 particles using image J software.

X-ray diffraction spectra are recorded on an MPD Pro Panalytical spectrometer using Co Ka radiation with a Kapton film holder. Before sample preparation, a small ring of grease is drawn on the Kapton film. For sample preparation, a highly concentrated solution of nanocrystals dispersed in pentane is drop cast onto Kapton foil within the previously mentioned grease ring. When nanocrystal film is dry, a second piece of Kapton film is placed on top. This second piece becomes stuck to the first piece due to the presence of the grease ring. The sealed Kapton films are then placed in a holder and brought out of the glovebox for XRD analysis.

Solid-state NMR experiments are recorded on a Bruker Avance III 400 spectrometer. Samples are packed into 3.2 mm zirconia rotors inside an argon-filled glovebox. The rotors are spun between 8 to 18 kHz at room temperature. For 1H MAS and 13C CP (direct polarization) MAS experiments, a small flip angle (~30°) is used with recycle delays of 5 s and 10 s, respectively. $^{31}$P Hahn-echo is performed with a recycle delay of 60 s and 6 s, respectively. $^{31}$C CP-MAS and $^{31}$P CP-MAS spectra are recorded with a recycle delay of 2 s.
and contact times of 2 ms, 2 ms and 3 ms, respectively. All chemical shifts for $^1$H and $^{13}$C are relative to TMS. $^{31}$P chemical shifts are referenced to an external 85% H$_3$PO$_4$ sample.

XPS measurements are recorded on a Thermo Electron Kα spectrometer with a base pressure of $5 \times 10^{-9}$ mbars. For high-resolution spectra, a pass energy of 20 eV is used and charging effect is neutralized with a dual e⁻/Ar⁺ source. The Cls core peak of adventitious carbon at 285.0 eV is used as an internal energy reference. The data are treated with Casaxps using Gaussian–Lorentzian combinations (GL30) for the fits and Scofield photoionization cross-section [32], corrected for the analysis depth and the analyzer’s transmission function, for quantification.

UV–Visible Absorbance spectra are measured by using a Perkin Elmer lambda 35 scanning spectrometer with the sample in a 2 mm cells. Emission spectra are recorded with excitation laser centered at 402 nm (Nichia-MLVH 300E). The light is then dispersed by a monochromator PL Acton SpectraPro 2500i. The detection is done 90° by CDD camera (Spec-10:100 BR/LN). Acquisition is performed by Winspec32 software.

For determinations of quantum yield (QY), the comparative method outlined by Williams et al. is used. The internal standard used is rhodamine 6G.

For time resolved emission measurements (TR emission) experiments are performed using 1.5 ps laser pulses generated by a tunable mode-locked Ti:Sa laser. A pulse picker is used to reduce the repetition rate from 80 MHz to 0.04 MHz and a second harmonic generation unit converted the excitation wavelength down to 390 nm. The laser beam is focused onto the cuvette on a 1/e diameter spot of ~100 μm and an average power of 50 μW. The PL signal is dispersed by a f#-6.5 spectrometer and detected as a function of time by a synchro-scan Hamamatsu streak camera with an overall temporal resolution of 35 ns.

3. Results and Discussion

Cd$_3$P$_2$ NCs are prepared using our already published protocol based on Cd(OAc)$_2$(OcAm)$_2$ (OcAm = octylamine) and tris(trimethylsilyl)phosphine (PTMS) as reagents [26]. Cd$_3$P$_2$ cores synthetized with octylamine cannot be precipitated via centrifugation so hexadecylamine at the surface. Regarding cadmium, the Cd 3d doublet is found at 404.12 eV, 35 scanning spectrometer with the sample in a 2 mm cells. Emission spectra are recorded for quantification.

The CP spectrum of Cd$_3$P$_2$ shows P signal post shelling with one broad peak centralized around 225 ppm (seen in Figure 1b). The presence of Cd$_3$P$_2$ cores which are roughly spherical in shape and monodisperse with average size of 3.6 ± 0.4 nm ($\sigma$ = 11%) matching well with previous reports [26].

Our Zn$_3$P$_2$ shelling protocol (Scheme 1) relies on the use of novel zinc precursor bis-diisopropylacetamidinato zinc(II), referred to as zinc(II) amidinate. This complex is selected for its high reactivity which proved to be highly relevant for the passivation of InP QDs and for the synthesis of Zn$_3$P$_2$ NCs [33]. Briefly, purified Cd$_3$P$_2$ cores are combined in a round bottom (RB) flask with Zn(amidinate)$_2$ and oleylamine as the solvent. The RB flask is then heated to 180°C, at temperature, P(SiMe$_3$)$_3$ dissolved in oleylamine is slowly added dropwise. Key to the syntheses’ success is the removal of excess Cd precursor from the Cd$_3$P$_2$ cores, via centrifugation, before shelling. If Cd$_3$P$_2$ cores are used as synthesized, the excess Cd precursor reacts with P(SiMe$_3$)$_3$ preferentially, leading to the formation of additional Cd$_3$P$_2$ NCs. Figure 1a shows a TEM image of Cd$_3$P$_2$/Zn$_3$P$_2$ NCs grown from Cd$_3$P$_2$ cores stabilized with hexadecylamine. The shape of Cd$_3$P$_2$/Zn$_3$P$_2$ NCs is uniformly spherical in nature, similar to the Cd$_3$P$_2$ cores. The average size of Cd$_3$P$_2$/Zn$_3$P$_2$ NCs is 5.7 ± 0.6 nm ($\sigma$ = 11%) with a shell width of ca 1.0 nm (Figure 1b). The composition of these shelled NCs is determined using ICP-MS, EDX, and XPS and all these techniques give consistent results close to Cd$_3$P$_2$/Zn$_3$P$_2$ (Table S1).

![Scheme 1](image-url)

**Scheme 1.** Scheme detailing the synthesis of a Zn$_3$P$_2$ shell on top of Cd$_3$P$_2$ cores.
Table 2022 Nanomaterials 2022, 12, x FOR PEER REVIEW

which is consistent with a phosphorus environment. The Zn 2p region displays 1 doublet (Figure S3b). This spectrum shows P signal post shelling with one broad peak centralized around 128.1–129.0 eV, is assigned to Cd-P/Zn-P bonding within the nanoparticles [36]. The binding energy of the second doublet, found at 132.8–133.7 eV, is close to the values reported for phosphorus in nitrogen or oxygen environment. Therefore, consistently with previous work of Bawendi which showed the possibility of growing CdS (cubic structure) tetrapods on cubic CdP seeds [29]. This is highlighting, once again, the important role that crystallographic matching plays on successful growth of heterostructures, and in our case, in the growth of Zn3P2 shell with high uniformity and robustness.

The optical properties of Cd3P2 and Cd3P2/Zn3P2 are characterized using absorbance and emission (steady state and time resolved) spectroscopies. The absorbance and emission spectra of Cd3P2 cores (blue) and Cd3P2/Zn3P2 (red) core-shell QDs are seen in Figure 2a.

Figure 1. (a) TEM image of Cd3P2/Zn3P2 core-shell NCs. (b) Histograms of measured NC sizes for Cd3P2 cores and Cd3P2/Zn3P2 core-shell NCs.
The absorbance spectra of Cd$_3$P$_2$ cores demonstrates a broad hump from its onset point, 710 nm, with an absorption maximum of 644 nm, matching well with previous reports on this particle size [26]. For Cd$_3$P$_2$/Zn$_3$P$_2$ NCs, the absorbance spectrum is similarly broad from its onset, 720 nm, with an absorbance maximum of 649 nm. The emission spectra of Cd$_3$P$_2$ and Cd$_3$P$_2$/Zn$_3$P$_2$ NCs taken at an excitation wavelength of 430 nm are also seen in Figure 2a. Cd$_3$P$_2$ cores demonstrate an emission maximum of 729 nm with a full width at half maximum (FWHM) of 80 nm, consistently with previous reports [26]. Cd$_3$P$_2$/Zn$_3$P$_2$ core-shells have an emission maximum of 736 nm with a FWHM of 90 nm, giving a 7 nm redshift relative to Cd$_3$P$_2$ cores. These observations are consistent with previous reports for CdSe/ZnS [10] or the related Cd$_3$P$_2$/ZnS QDs [26] can be assigned to the leakage of the exciton into the shell material.

![Figure 2](image)

**Figure 2.** (a) Absorbance and emission of Cd$_3$P$_2$ cores (blue) and Cd$_3$P$_2$/Zn$_3$P$_2$ (red) core-shell NCs sealed in gas tight cuvettes under an Ar atmosphere. (b) Time-resolved emission spectra of Cd$_3$P$_2$ cores (blue) and Cd$_3$P$_2$/Zn$_3$P$_2$ (red) core-shell NCs and (d) graph showing changes in absorbance and emission maxima of Cd$_3$P$_2$ (blue triangles) and Cd$_3$P$_2$/Zn$_3$P$_2$ (red squares) NCs upon exposure to air over a 16-day period.

The higher bandgaps of Zn$_3$P$_2$ (1.5 eV) compared to Cd$_3$P$_2$ (0.5 eV) should lead to similar absorbance and emission maxima post-shelling due to their type I band alignment [6]. The minor absorbance and emission redshifts (5–10 nm) observed for Cd$_3$P$_2$/Zn$_3$P$_2$ are consistent with a slight overlap of the exciton into the shell as described by previous reports of type I core-shell QDs (CdSe/ZnS, InP/ZnSe) [10,38].

The QYs of Cd$_3$P$_2$ and Cd$_3$P$_2$/Zn$_3$P$_2$ NCs are calculated by the comparative method using rhodamine 6G as a reference. The QYs of Cd$_3$P$_2$ and Cd$_3$P$_2$/Zn$_3$P$_2$ NCs are, respectively, 52% and 45%. As this slight difference is within the uncertainty of the comparative method, no significant modification of the QY can be observed post-shelling. This result is reminiscent to our previous work on ZnS coating [26], where the QY of the Cd$_3$P$_2$ cores (around 50%) is not increased or impacted by the presence of a layer of ZnS.

To gain insight into the fundamental optical properties of Cd$_3$P$_2$/Zn$_3$P$_2$ NCs, time resolved emission spectroscopy is used. All NCs require biexponential fits, with time constants summarized in Table S3. Figure 2b shows the fitted time resolved emission data of Cd$_3$P$_2$/Zn$_3$P$_2$ and Cd$_3$P$_2$ NCs for reference. The two emission components of Cd$_3$P$_2$ have lifetimes of 110 ns ($\tau_1$) and 290 ns ($\tau_2$) with contributions of 75% and 25%, respectively (average 155 ns). These $\tau_1$ and $\tau_2$ values are consistent with an emission from two different types of defects, consistently with previous results for both NCs and bulk.
Cd₃P₂ [30]. After shelling, the two emission components of Cd₃P₂/Zn₃P₂ have lifetimes of 140 ns and 290 ns, with contributions of 25% and 75%, respectively (average 253 ns). The difference between the lifetimes before and after shelling is not significant. However, after shelling, the contribution from the first decay component has decreased drastically, 75% to 25%. We assume that the shelling process has led to a partial passivation of the states responsible of the τ₁ component. The chemical nature of these optically active defects might be related to the surface oxidized phosphorus species, PO₄, as seen in the ³¹P NMR. Similar observations are seen in the optical properties of InP/ZnX (X = S, Se) [39], highlighting the detrimental nature oxides can play on NC optical properties. However, compared to well-studied materials such as CdSe, the band structure of both Cd₃P₂ and Zn₃P₂ is not well understood [27,40]. Long-lived emissive transitions in Cd₃P₂ QDs have been described in the literature but their cause is still unknown [40]. In our case, the second long-lived transition is not altered by the presence of the Zn₃P₂ shell, its origin could be an intraband transition within the Cd₃P₂ bandgap, and therefore from an energy perspective, it is unaffected by the higher bandgap Zn₃P₂ shell. To fully understand the origin of these emissive transitions, more research is needed.

The stability of Cd₃P₂ and Cd₃P₂/Zn₃P₂ optical properties with respect to air was monitored using absorbance and emission spectroscopy. Figure 2c,d show respectively the absorbance and the emission maxima of Cd₃P₂ and Cd₃P₂/Zn₃P₂ exposed to air over an 18-day period. After 1 day of air exposure, the absorbance and the emission of Cd₃P₂ NCs strongly blueshift, demonstrating the high sensitivity of Cd₃P₂ cores to air. In contrast, the presence of a Zn₃P₂ shell clearly improves the optical stability of Cd₃P₂ as reliable QD absorbance and emission remains essentially unchanged for up to 14 days post exposure to air. In comparison, assembly of Cd₃P₂ QDs embedded in silica, showed a stability of only 2.5 days in buffer solution [31].

In summary, looking for new directions towards the successful shelling for Cd₃P₂ and potentially other II–V materials, Zn₃P₂ was explored for the first time as a shelling material. A new synthetic procedure was developed through the use of Zn(κ-amidinate)₂ and P(SiMe₃)₃ as zinc and phosphorus precursors, respectively. Low/high resolution TEM in conjunction with XRD measurements demonstrated that Zn₃P₂ shells could be easily grown onto Cd₃P₂ cores. Cd₃P₂/Zn₃P₂ core-shell NCs demonstrated nearly identical absorbance/emission maxima and QY compared to Cd₃P₂ core. Importantly, the Cd₃P₂/Zn₃P₂ core-shell NCs had significantly higher air stability demonstrating stable QD absorbance and emission up to 14 days post air exposure, compared to Cd₃P₂ cores which lost both 1 day post air exposure. This work represents thus a required step towards their practical use in a range of visible/IR based optoelectronic devices.

For the large majority of applications where semiconductors NCs are currently utilized, their true exploitation began after the development of robust shelling materials and strategies. Zn₃P₂ exhibiting a tetragonal structure and a bandgap (1.5 eV) higher than the majority of II–V materials, the shelling developed here should be broadly applicable to other II–V tetragonal QDs (Cd₃As₂, Cd₃Zn₃As₂) analogous to shelling common place II–VI and III–V cubic QDs (CdSe, CdS, InP) with ZnS. With this synthesis, the next generation of II–V materials can be unlocked for exploration, from fundamental optics to applied materials.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/10.3390/nano12193364/s1, Figure S1: Low (left) and high (right) resolution transmission electron microscopy images of Cd₃P₂ cores synthesized with hexadecylamine as the surfactant; Figure S2: High resolution transmission electron microscopy (a) of Cd₃P₂/Zn₃P₂ nanocrystals and XRD patterns (b) of Cd₃P₂ cores (blue), Cd₃P₂/Zn₃P₂ (red), the relevant reflections are highlighted for Cd₃P₂ 00-002-1182 and Zn₃P₂ 01-002-1264. The * symbol denotes reflections that are caused by the kapton film; Figure S3: Magic Angle Spinning NMR of Cd₃P₂/Zn₃P₂: (a) 13C CP MAS NMR spectra of Cd₃P₂/Zn₃P₂, (b) 31P Hahn-echo MAS NMR spectra of Cd₃P₂/Zn₃P₂; Figure S4: High resolution XPS of Cd₃P₂/Zn₃P₂: (a) P 2p and Zn 3s core peaks; (b) Cd 3d core peaks, the detection of a N 1s peak at ca. 399.0 eV is due to the presence of nitrogen atoms in the oleylamine
ligands; (c) Zn 2p core peaks. The presence of carbon and oxygen is also detected through O 1s and C 1s core peaks (not shown here); Table S1: Composition of synthesized nanocrystals from ICP-MS, EDX, and XPS measurements. XPS compositions were determined from the P 2p, Zn 3s and Cd 3d core peaks; Table S2: XRD peak maxima and full width at half maxima for the (220) plan of CdS and CdS/CdSe/ZnSe core/shell/shell type II nanocrystals.

Author Contributions: B.F.P.M.: investigation, conceptualization, visualization, writing—original draft; R.A.S.: investigation, conceptualization, validation; D.L.: investigation, resources, writing—original draft; W.-S.O.: investigation; K.B.: validation, writing—review & editing; C.M.: investigation, resources, writing—original draft; B.W.: resources, writing—review & editing; Y.T.: investigation, resources, writing—original draft; H.M.: resources, writing—review & editing; B.C.: conceptualization, writing—review & editing; C.N.: supervision, project administration, funding acquisition, writing—original draft, conceptualization, visualization; all authors have read and agreed to the published version of the manuscript.

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