Synthesis of luminescent core/shell α-Zn₃P₂/ZnS quantum dots

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Experimental Details

Characterization

X-ray Diffraction (XRD)

XRD characterization was performed using a Bruker AXS D8 DISCOVER GADDS Microdiffactometer with Cu Kα radiation (λ = 0.154 nm). Samples were prepared by drop casting a concentrated solution of nanoparticles in hexanes onto a 1 cm x 1 cm <100> silicon substrate inside of a nitrogen filled glovebox. XRD scans were collected using an incident angle of ω = 3°. XRD peaks were indexed using GSAS-II software.1

Transmission Electron Microscopy (TEM)

TEM samples were prepared on 300 mesh formvar/carbon grids (Ted Pella, FCF300-Cu-UA). Bright field images were obtained using a Tecnai Spirit 120kV TEM. Superlattices of Zn₃P₂ nanoparticles were prepared according to a procedure by Sainato et al.2 The particle size distribution of each sample was determined using the ImageJ software.3

HRTEM images were taken using a FEI Titan Themis 200 kV TEM. STEM-EELS and STEM-EDX elemental maps were acquired with a Hitachi HD2700C dedicated STEM with a probe Cs corrector at an accelerating voltage of 200 kV. For HRTEM and STEM experiments, samples were prepared by drop casting a dilute filtered solution of nanoparticles dispersed in hexanes onto a TEM grid.

Absorbance Spectra

Absorbance spectra were obtained using an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. The nanoparticles were dispersed in carbon tetrachloride for measurement.
Photoluminescence (PL)

For solution samples, PL spectra were obtained using a Photon Technology International QuantaMaster 4 fluorescent spectrometer. The nanoparticles were dispersed in hexanes for measurement.

For thin film samples, PL and time-resolved photoluminescence (TRPL) measurements were performed with a home-built confocal microscopy setup. A 400 nm femtosecond laser source (Coherent Chameleon) with a repetition rate of 80MHz was used as excitation light source. An objective (NA 0.55) was used for focusing the laser into a spot with diameter ~2 μm. The emitted light was directed into a spectrograph (Andor SR500i, with a grating with 150 l/mm groove density, 1250 nm blazed wavelength). A thermal-electric cooled CCD array was used to measure the PL spectra. The TRPL measurements were done by a time-correlated single photon counting (TRSPC) module (PicoQuant TimeHarp-260) and an avalanche photodiode (MPD SPAD).

X-ray Photoelectron Spectroscopy (XPS)

XPS data was measured using a Versa Probe II XPS from Physical Electronics with Al Kα source operated at 50 W 15 kV with a 200 μm spot size. Samples were prepared by drop casting a solution of nanoparticles onto a 1 cm x 1 cm glass slide (Thin Film Devices).
Supplementary Figures

Figure S1. XRD patterns obtained for $\alpha$-Zn$_3$P$_2$ (reference: ICSD-603896) nanoparticles grown for 1 hour, 2 hours, and 4 hours. Nanoparticles were grown following injection of P(SiMe$_3$) at 220°C. In some cases, we observed the formation of a hydrated zinc phosphate tetrahydrate (triangle, reference: ICSD-34869) and zinc hydroxide (asterisk, reference: ICSD-15008).

Figure S2. XRD patterns obtained for $\alpha$-Zn$_3$P$_2$ nanoparticles (reference: ICSD-603896) grown at 220°C for 2 hours following injection of P(SiMe$_3$)$_3$ at 160°C, 180°C, 200°C, and 220°C. In some cases, we observed the formation of zinc phosphate tetrahydrate (reference: ICSD-34869) and zinc hydroxide (reference: ICSD-15008).
Figure S3. XRD patterns obtained for α-Zn₃P₂ nanoparticles (reference: ICSD-603896) grown for 2 hours following injection of P(SiMe₃)₃ at 220°C using (a) zinc acetate and (b) zinc oleate. In both cases, we observed the formation of zinc phosphate tetrahydrate (reference: ICSD-34869) or zinc hydroxide (reference: ICSD-15008).

Figure S4. Bright field image for core/shell Zn₃P₂/ZnS nanocrystals synthesized from Method 1.
Figure S5. XRD data for Zn$_3$P$_2$/ZnS core/shell nanocrystals grown from Method 1 (red), using elemental sulfur and zinc acetate, and Method 2 (green), from zinc oleate and thioacetamide. The orange asterisks correspond to peaks for ZnO (ICSD-193696).

Figure S6. (a) HAADF-STEM image for a cluster of Zn$_3$P$_2$/ZnS nanocrystals. (b) Elemental mapping of the cluster of nanocrystals, with P, Zn, and S signals overlaid. (c), (d), and (e) show elemental maps for individual elements Zn, P, and S, respectively.
Figure S7. XPS data obtained at the sulfur (S) edge for Zn$_3$P$_2$/ZnS nanocrystals. The S(2p3/2) peak present at 162 eV that appeared following shelling of Zn$_3$P$_2$ with ZnS is characteristic of zinc sulfide.

Figure S8. Photos of (a, b) core and (c) core/shell nanoparticles suspended in hexanes. Photos show samples exposed to air (a) one day after exposure and (b, c) one week after exposure. The loss of color in the core nanoparticle solution indicated oxidation of the nanocrystals, which did not occur on core/shell nanocrystals over the same length of time. The core/shell particles are dispersed at a lower concentration than the core-only particles – hence the lighter shade.
Figure S9. Time resolved photoluminescence studies performed on a thin film of Zn₃P₂/ZnS nanocrystals deposited from a dispersion of nanocrystals in toluene at 77 K. The estimated lifetime of 0.18 ± 0.08 ns was obtained from the average $\tau$ values from three measurements (a, b, c at different locations) on the same film.
Figure S10. Time resolved photoluminescence studies performed a thin film deposited from Zn$_3$P$_2$/ZnS nanocrystals at RT. The estimated lifetime of $0.18 \pm 0.15$ ns was obtained from the average $\tau$ values from two measurements (a,b at different locations) on the same film.
Figure S11. Photographs of Zn₃P₂ growth within one minute of injection of tris(trimethylsilyl)phosphine. The color of the reaction solution rapidly changed from clear and colorless to dark red within one minute of injection.

Theoretical Calculations

Calculation of Bohr Radius

The Bohr radius of Zn₃P₂ is given by

\[ a_{Bohr} = \varepsilon_r \left( \frac{m}{\mu} \right) a_0 \]

where \( \varepsilon_r = 15.3 \text{ F/m} \) for Zn₃P₂, \( m = \text{mass} \), \( \mu = \text{the reduced mass} \) \((m_e = 0.09, m_h = 0.95)\), and \( a_0 = 0.053^4 \). This provides \( a_{Bohr} = 9.87 \text{ nm} \) for Zn₃P₂. The estimated band gap \( E_g \) can then be calculated within this range of quantum confinement is given by

\[ E_g = E_{g,0} + \frac{\hbar^2 \pi^2}{2\mu R^2} \]

where \( E_{g,0} = 1.5 \text{ eV} \) for Zn₃P₂, \( \hbar = 1.054571817 \times 10^{-34} \text{ J·s} \), and \( R = \text{the radius of the nanoparticle} \).
Figure S12. Predicted band gap for quantum confined Zn$_3$P$_2$. Calculations show that Zn$_3$P$_2$ has a Bohr radius of 10 nm. The asterisk and dashed line indicate experimental data.
<table>
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<th>Diameter (nm)</th>
<th>Radius (nm)</th>
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<th>Wavelength $\lambda$ (nm)</th>
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Calculation of Shell Precursor Volumes

The approximate amount of sulfur added per shelling experiment was determined using the following calculation.

Assumptions:

- The particles are spherical with a volume of \( V = \frac{4\pi}{3} r^3 \).
- The ligands take up 30% of the nanoparticles’ mass.
- The bulk densities of the \( Zn_3P_2 \) (4.55 g/cm\(^3\)) and \( ZnS \) (4.09 g/cm\(^3\)) are equal to the densities of \( Zn_3P_2 \) nanoparticles and \( ZnS \) shells.
- Each monolayer of \( ZnS \) is 0.3 nm thick.

Measured Parameters

- The mass of the nanoparticles was measured following vacuum drying of the nanoparticles in a glass vial.
- The average diameter of the nanoparticles was determined from LRTEM image analysis using ImageJ.

Sample Calculation for a Single Monolayer of \( ZnS \)

The following sample calculation determines the amount of \( Zn \) and \( S \) precursors required to provide two shelling layers on 100 mg of 7 nm nanoparticles. The concentration of the \( Zn \) precursor is 0.02 M and the concentration of the \( S \) precursor is 0.04 M.

1. Determine the number of nanoparticles.

The volume of each nanoparticle is given by
\[
V = \frac{4}{3}\pi \left(\frac{7}{2} nm\right)^3 = 179.5 \text{ nm}^3
\]

Given the density of Zn$_3$P$_2$, and assuming that the ligands take up 30% of the particles’ mass, the mass of one nanoparticle is equal to

\[
m_{Zn_3P_2} = (179.5 \text{ nm}^3) x \left(4.55 \frac{g}{cm^3}\right) x \left(\frac{1 \text{ cm}^3}{1 \times 10^{21}\text{ nm}^3}\right) x (100/130) = 6.29 \times 10^{-19} g
\]

The number of nanoparticles is therefore equal to

\[
n_{Zn_3P_2} = \frac{0.1 g}{6.29 \times 10^{-19} g} = 1.59 \times 10^{17}
\]

2. Determine the volume required to add one monolayer of ZnS.

Assuming that one ZnS monolayer is 0.3 nm thick, the volume of ZnS required for one nanoparticle is equal to

\[
V = \frac{4}{3}\pi (3.5 \text{ nm} + 0.3 \text{ nm})^3 - 179.5 \text{ nm}^3 = 50 \text{ nm}^3
\]

For \(n\), the total mass of ZnS to add is given by

\[
m_{ZnS} = (50.26 \text{ nm}^3) x \left(4.09 \frac{g}{cm^3}\right) x \left(\frac{1 \text{ cm}^3}{1 \times 10^{21}\text{ nm}^3}\right) x (1.59 \times 10^{17}) = 3.3 \times 10^{-2} g
\]

For a 0.04 M solution of S precursor and 0.02 M solution of Zn precursor, the total volume required is therefore

\[
V_{S,1} = 3.3 \times 10^{-2} g x \frac{1 \text{ mol}}{97.474 \text{ g}} x \left(\frac{1 L}{0.04 \text{ mol}}\right) = 8.39 \text{ ml S}
\]

\[
V_{Zn,1} = 3.3 \times 10^{-2} g x \frac{1 \text{ mol}}{97.474 \text{ g}} x \left(\frac{1 L}{0.02 \text{ mol}}\right) = 15.2 \text{ ml Zn}
\]
Calculation of Lifetimes

We calculated the average lifetime from a biexponential fit of photoluminescence intensity $I$ (a.u.) with respect to time $t$ (ns):

$$ I = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} $$

where $A_1$ and $A_2$ are the preexponential factors, and $\tau_1$ and $\tau_2$ are the lifetimes provided by the fit.

We fitted $I$ from measurements at different locations on the same film at 77 K (Figure S9) and RT (Figure S10). Results have been summarized in Table S2.

<table>
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<th>Conditions</th>
<th>$A_1$</th>
<th>$\tau_1$ (ns)</th>
<th>$A_2$</th>
<th>$\tau_2$ (ns)</th>
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From this data, we then calculated the average lifetime $\tau_{avg}$ considering from the following formula:

$$ \tau_{avg} = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2} $$

where $\alpha$ is the normalized pre-exponential factor such that

$$ \alpha_i = \frac{A_i}{\sum A_i} $$

From the data obtained from our biexponential fits, we calculated the mean $\tau_{avg}$ to be $0.18 \pm 0.15$ ns at RT and $0.18 \pm 0.08$ ns at 77 K. Results are summarized in Table S3.
Table S3. Calculations of the Average Lifetime

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References:


