

# Ion Exchange Synthesis of III-V Nanocrystals

Brandon J. Beberwyck and A. Paul Alivisatos

## Supporting Information

### Materials:

All chemicals were used as received without purification. Cadmium oxide (CdO, 99.99%, Sigma Aldrich), oleic acid (90%, Sigma Aldrich), 1-octadecene (ODE, 90%, Sigma Aldrich), tris(trimethylsilyl)phosphine ((TMS)<sub>3</sub>P, 95%, Sigma Aldrich), tris(trimethylsilyl)arsine ((TMS)<sub>3</sub>As, 99%, Nanomeps), cadmium nitrate tetrahydrate (99%, Sigma Aldrich), sodium hydroxide (98%, Fisher), myristic acid (99%, Sigma Aldrich), tri-n-octylphosphine (TOP, 97%, Strem), indium chloride (InCl<sub>3</sub>, 99.999%, Strem), gallium chloride (GaCl<sub>3</sub>, 99.999%, Sigma Aldrich), 1-butanol (99.4%, EMD), methanol (99.9%, Fisher), acetone (99.9%, Sigma Aldrich, dried over 4Å molecular sieves), anhydrous solvents including chloroform (99%, Sigma Aldrich), methanol (99.8% Sigma Aldrich), ethanol (99.5%, Sigma Aldrich), octylamine (99%, Sigma Aldrich), carbon tetrachloride (99.5%, Sigma Aldrich).

All manipulations were performed using standard air-free techniques on a Schlenk line (Ar, vacuum P<100 mTorr) or in a glovebox (Ar, O<sub>2</sub><2 ppm).

### Cd<sub>3</sub>As<sub>2</sub> nanocrystals:

Cd<sub>3</sub>As<sub>2</sub> nanocrystals were synthesized according to a literature procedure.<sup>1</sup> Cadmium (II) myristate was prepared as previously described,<sup>2</sup> washed with methanol 3x, recrystallized once from butanol, and vacuum dried overnight. In a typical Cd<sub>3</sub>As<sub>2</sub> synthesis, 1 mmol Cd (II) myristate was combined with 5 mL ODE and heated to 100 °C under vacuum for 1 hour. The mixture was then heated to 175 °C under Ar and 0.05 mmol (TMS)<sub>3</sub>As in 0.8 mL TOP was rapidly injected. After 20 minutes, a syringe pump slowly added an additional amount of a stock solution of 0.5 mmol (TMS)<sub>3</sub>As in 10 mL TOP at a rate of 1.5 mL per hour. For the smaller 3 nm particles, 1.5 mL of this stock solution was added while for the larger 4.5 nm particles the entire 10 mL stock was added. After the desired particle size was reached, the reaction was cooled to room temperature and the raw solution was transferred into a glovebox. The Cd<sub>3</sub>As<sub>2</sub> nanocrystals were cleaned 3x by precipitation and redissolution using chloroform and acetone as the solvent and nonsolvent, respectively.

### Cd<sub>3</sub>P<sub>2</sub> nanocrystals:

Cd<sub>3</sub>P<sub>2</sub> nanocrystals were synthesized according to a literature procedure<sup>3</sup> with modification. Briefly, 0.3 mmol CdO, 2 mmol oleic acid, and 4 mL ODE were combined in a 25 mL flask and heated to 210 °C under Ar to form a clear complex. Next, 0.1 mmol (TMS)<sub>3</sub>P in 0.5 mL ODE was rapidly injected and the heating mantle was immediately removed to cool the solution to room temperature. The raw solution was transferred into a glovebox and the Cd<sub>3</sub>P<sub>2</sub> nanocrystals were cleaned 3x by precipitation and redissolution using chloroform and acetone as the solvent and nonsolvent, respectively.

### In<sup>3+</sup> ion exchange:

The procedure for the In<sup>3+</sup> ion exchange of Cd<sub>3</sub>As<sub>2</sub> and Cd<sub>3</sub>P<sub>2</sub> is similar. A 1 M InCl<sub>3</sub>:TOP stock solution was prepared by combining 10 mmol InCl<sub>3</sub> and 10 mL TOP in a flame dried 25 mL flask and heated to 270 °C under Ar for 1 hour, cooled, and transferred into the glovebox. In a typical In<sup>3+</sup> ion exchange reaction, 1 mL of the 1 M InCl<sub>3</sub>:TOP stock solution and an additional 1 g TOP were loaded into a flame dried 25 mL flask under Ar atmosphere. The solution was heated to 270 °C under Ar and either Cd<sub>3</sub>P<sub>2</sub> or Cd<sub>3</sub>As<sub>2</sub> nanocrystals (7.5 μmol Cd<sup>2+</sup> (100x excess In:Cd) as determined by ICP-AES) dissolved in 0.83 g TOP were rapidly injected into the ion exchange solution. The reaction was kept at 270 °C for 15 minutes before the heating mantle was removed and the reaction cooled to room temperature. The raw solution was transferred into a glovebox and 2 mL chloroform and 10 mL 1:1 EtOH:MeOH solution was added to induce flocculation. The solution was centrifuged and the supernatant discarded. The precipitate was redispersed in chloro-

form and the cleaning procedure repeated an additional 2-3x. The final precipitate was dispersed in chloroform and passed through a 0.2  $\mu\text{m}$  PTFE syringe filter.

#### **Ga<sup>3+</sup> ion exchange:**

The procedure for the Ga<sup>3+</sup> ion exchange of Cd<sub>3</sub>As<sub>2</sub> and Cd<sub>3</sub>P<sub>2</sub> is similar. A 1M GaCl<sub>3</sub>:TOP stock solution was prepared in a glovebox by combining 10 mmol GaCl<sub>3</sub> with 10 mL TOP and stirred overnight at room temperature. In a typical Ga<sup>3+</sup> ion exchange reaction, 1 mL of the 1 M GaCl<sub>3</sub>:TOP stock solution and an additional 1 g TOP were loaded into a flame dried 25 mL flask under Ar atmosphere. The solution was heated to 300 °C under Ar and either Cd<sub>3</sub>P<sub>2</sub> or Cd<sub>3</sub>As<sub>2</sub> nanocrystals (7.5  $\mu\text{mol}$  Cd<sup>2+</sup> (100x excess Ga:Cd) as determined by ICP-AES) dissolved in 0.83 g TOP were rapidly injected into the ion exchange solution. The reaction was kept at 300 °C for 15 minutes before the heating mantle was removed and the reaction cooled to room temperature. The raw solution was transferred into a glovebox and 2 mL chloroform and 10 mL 1:1 EtOH:MeOH solution was added to induce flocculation. The solution was centrifuged and the supernatant discarded. The precipitate was redispersed in chloroform and the cleaning procedure repeated an additional 2-3x. In many situations, alcohols caused the flocculation of the nanocrystals as well as precipitated large amounts of white, residual Ga-complex. When this occurred, a few drops of octylamine were added to the solution to redissolve the Ga-complex and the cleaning procedure continued. The final precipitate was dispersed in chloroform and passed through a 0.2  $\mu\text{m}$  PTFE syringe filter.

#### **Absorption Spectroscopy:**

Absorbance spectra were acquired using a Shimadzu 3600 spectrophotometer with 1nm increments with solvent background subtraction. For absorbance measurements, the 4.5 nm Cd<sub>3</sub>As<sub>2</sub> nanocrystals were dispersed in carbon tetrachloride and the remaining samples were dispersed in chloroform.

#### **Electron Microscopy:**

TEM grids were prepared by drop-casting dilute solutions of nanocrystals onto amorphous carbon on 400 mesh Cu grids (Electron Microscopy Sciences) for low-resolution or ultrathin carbon on holey carbon film on 400 mesh Au grids (Ted Pella) for high resolution. Low resolution images were acquired using a 200 kV LaB<sub>6</sub> FEI G20 20 Tecnai and high-resolution images were acquired on a 200 kV FEG FEI monochromated F20 UT Tecnai. Particle sizes were measured using ImageJ (<http://rsbweb.nih.gov/ij/>).

#### **X-ray Diffraction:**

XRD scans were collected on a Bruker GADDS Hi-Star D8 diffractometer with Co K $\alpha$  ( $\lambda=1.790$  Å) operating at 45 kV/35 mA. Samples were prepared in a glovebox by drop casting concentrated nanocrystal solutions onto a silicon crystal plate. Air sensitive samples were measured using an airtight silicon crystal specimen holder (Bruker) to minimize air exposure. Patterns were background subtracted by the Bézeir method and compared to reference patterns from the Inorganic Crystal Structure Database (ICSD).

#### **Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES):**

Cd<sup>2+</sup> concentrations of the Cd<sub>3</sub>P<sub>2</sub> and Cd<sub>3</sub>As<sub>2</sub> nanocrystal solutions and residual Cd<sup>2+</sup> concentrations in the ion exchanged nanocrystals were determined using an Optima 7000 DV ICP-AES (Perkins Elmer). Cd, Ga, In, and As ICP/DCP standard solutions (Fluka) were serially diluted to prepare a linear calibration curve spanning several orders of magnitude, ensuring sample concentrations fell within this linear range. Samples were prepared by drying nanocrystals solution under Ar and the solids digested using concentrated nitric acid (65%, TraceSELECT® Ultra, Fluka). These solutions were subsequently diluted to 10 mL total volume with Milli-Q™ (Millipore) water and passed through a 0.2  $\mu\text{m}$  nylon syringe filter. Nitric acid concentrations were 2% wt/wt in all samples and standard solutions.

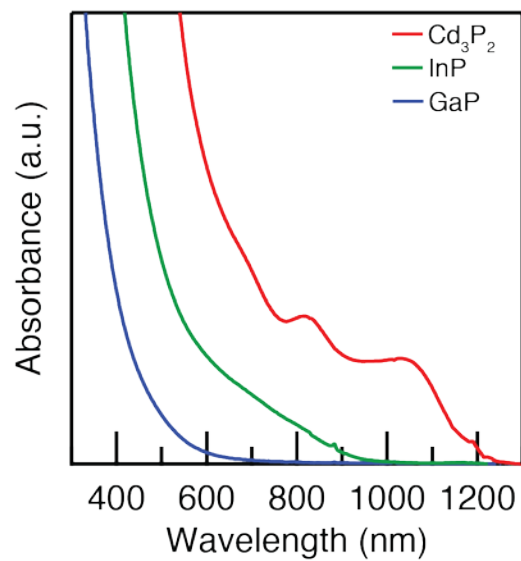


Figure S1. Absorption spectra of initial  $\text{Cd}_3\text{P}_2$  nanocrystals and those which have been exchanged to  $\text{InP}$  and  $\text{GaP}$ . The initial  $\text{Cd}_3\text{P}_2$  shows a bimodal size distribution leading to a broad absorption feature for the  $\text{InP}$ .

Table S1. ICP-AES results of Ga<sup>3+</sup> ion exchanges (300 °C for 15 min) and In<sup>3+</sup> ion exchanges (270 °C for 15 min) of Cd<sub>3</sub>As<sub>2</sub> and Cd<sub>3</sub>P<sub>2</sub> nanocrystals, normalized to Cd concentration. \*Note for the sequential exchanged InAs ,the higher In concentration is due to residual In from the exchange procedure.

Sample	Ga	In	As	Cd
In <sup>3+</sup> exchange of 3 nm Cd <sub>3</sub> As <sub>2</sub>	-	13.4	8	1
In <sup>3+</sup> exchange of 4.5 nm Cd <sub>3</sub> As <sub>2</sub>	-	15.8	11.4	1
Sequential In <sup>3+</sup> exchange of previously In <sup>3+</sup> exchanged 4.5 nm Cd <sub>3</sub> As <sub>2</sub>	-	70*	19.5	1
In <sup>3+</sup> exchange of 4.5 nm Cd <sub>3</sub> As <sub>2</sub> followed by surface etch <sup>4</sup>	-	15.8	10.6	1
In <sup>3+</sup> exchange of 3.5 nm Cd <sub>3</sub> P <sub>2</sub>	-	22.3	-	1
Ga <sup>3+</sup> exchange of 3 nm Cd <sub>3</sub> As <sub>2</sub>	4.7	-	4.8	1
Ga <sup>3+</sup> exchange of 4.5 nm Cd <sub>3</sub> As <sub>2</sub>	4.3	-	5.7	1
Ga <sup>3+</sup> exchange of 3.5 nm Cd <sub>3</sub> P <sub>2</sub>	8.8	-	-	1

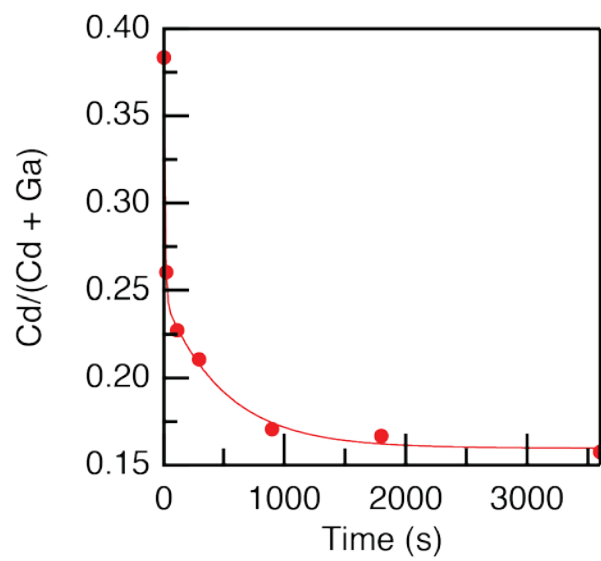


Figure S2. Ratio of residual Cd as a function of time for  $\text{Ga}^{3+}$  ion exchange of 4.5 nm  $\text{Cd}_3\text{As}_2$  at 300 °C.

Table S2. ICP-AES results of residual Cd after Ga<sup>3+</sup> ion exchange of Cd<sub>3</sub>As<sub>2</sub> as a function of temperature, time, and size.

T (°C)	t (min)	d (nm)	Cd/(Cd+Ga)
200	5	2.2	0.10
		3	0.17
		4.5	0.26
300	5	4.5	0.21
	60		0.16
350	5	4.5	0.17
	60		0.13

#### References:

- (1) Harris, D. K.; Allen, P. M.; Han, H.-S.; Walker, B. J.; Lee, J.; Bawendi, M. G. *J. Am. Chem. Soc.* **2011**, 133, 4676.
- (2) Chen, O.; Chen, X.; Yang, Y.; Lynch, J.; Wu, H.; Zhuang, J.; Cao, Y., *Angew. Chem., Int. Ed.* **2008**, 47, 8638.
- (3) Xie, R.; Zhang, J.; Zhao, F.; Yang, W.; Peng, X. *Chem. Mater.* **2010**, 22, 3820.
- (4) Battaglia, D.; Blackman, B.; Peng, X. *J. Am. Chem. Soc.* **2005**, 127, 10889.