Video Article Synthesis of $In_{37}P_{20}(O_2CR)_{51}$ Clusters and Their Conversion to InP Quantum Dots

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Abstract

This text presents a method for the synthesis of $In_{37}P_{20}(O_2C_{14}H_{27})_{51}$ clusters and their conversion to indium phosphide quantum dots. The $In_{37}P_{20}(O_2CR)_{51}$ clusters have been observed as intermediates in the synthesis of InP quantum dots from molecular precursors ($In(O_2CR)_{3}$, HO_2CR , and $P(SiMe_{3})_{3}$) and may be isolated as a pure reagent for subsequent study and use as a single-source precursor. These clusters readily convert to crystalline and relatively monodisperse samples of quasi-spherical InP quantum dots when subjected to thermolysis conditions in the absence of additional precursors above 200 °C. The optical properties, morphology, and structure of both the clusters and quantum dots are confirmed using UV-Vis spectroscopy, photoluminescence spectroscopy, transmission electron microscopy, and powder X-ray diffraction. The molecular symmetry of the clusters is additionally confirmed by solution-phase ³¹P NMR spectroscopy. This protocol demonstrates the preparation and isolation of atomically-precise InP clusters, and their reliable and scalable conversion to InP QDs.

Video Link

The video component of this article can be found at https://www.jove.com/video/59425/

Introduction

Colloidal semiconductor quantum dots have seen an acceleration in synthetic development over the previous three decades owing to their potential in a variety of optoelectronic applications including displays¹, solid-state lighting^{2,3}, biological imaging^{4,5}, catalysis^{6,7}, and photovoltaics^{8,9,10}. Given their recent commercial success in the area of wide-color gamut displays, the quantum dot market is expected to exceed 16 billion dollars by 2028¹¹. A significant shift in material focus from the II-VI (and IV-VI) to the III-V family has occurred in the last several years as the search for less toxic, Cd and Pb-free alternatives for use in highly distributed electronics applications has begun. Indium phosphide in particular has been identified as a leading drop-in replacement for CdSe¹². It has become apparent, however, that optimization of InP-based quantum dots is more difficult and does not always benefit from the same methods used for the more well-established chalcogenide materials. This is primarily because the nucleation and growth profile of InP nanoparticles follows a non-classical, two-step mechanism¹³. This mechanism is invoked due to the intermediacy of locally stable, atomically precise intermediates known as "magic-sized" clusters^{14,15,16}. In particular, In₃₇P₂₀(O₂CR)₅₁ has been identified as one key, isolable intermediate in the synthesis of InP from P(SiMe₃)₃, indium carboxylate, and carboxylic acid¹⁷.

The presence of this intermediate on the reaction coordinate has many tangible effects on the growth of InP nanostructures. The existence of cluster intermediates themselves invalidates classical concepts of nucleation and growth based on the La Mer model and means that optimizing reaction conditions such as concentration, temperature, and precursor may not achieve sufficiently uniform ensemble properties. Rather, it has been shown that the use of the InP cluster as a single-source precursor results in highly monodisperse quantum dots with narrow optical features¹³. Recent literature has suggested that monodispersity, however, is not the only factor limiting InP's parity with other optoelectronic materials¹⁸. Surface defects, oxidation, and alloying are critical factors still under intense research that will require significant innovation for optimized InP architectures^{19,20,21,22,23,24}. The atomically precise nature of clusters, such as In₃₇P₂₀(O₂CR)₅₁, makes them ideal platforms for probing the consequences of many post-synthetic surface modifications. Normally, ensemble inhomogeneity of nanoparticles makes determining surface and compositional effects difficult, but because the cluster of InP is known to be atomically precise, both compositionally and crystallographically, it is an ideal model system.

The synthesis of the $In_{37}P_{20}(O_2CR)_{51}$ cluster is no more difficult than the synthesis of more widely used nanoparticles such as CdSe, PbS, or ZnO. It requires only standard glassware, widely available chemicals, and basic knowledge of air-free Schlenk and glovebox techniques. The procedure itself can be done on the gram scale and with yields in excess of 90%. As we will show, the successful synthesis of InP cluster is not "magic" but rather an exercise in fundamentals. Pure reagents, dry glassware, proper air-free techniques, and attention to detail are all that is required to access this atomically precise nanocluster. Moreover, we also elaborate on ideal methods for its conversion to highly crystalline InP quantum dots with narrow size distributions.

Protocol

CAUTION: Proper personal protective equipment should be worn at all times and the material safety data sheet (MSDS) should be read for each chemical prior to use. All steps should be done air-free, because exposing clusters to air and/or water will degrade clusters or prevent proper formation. Any point at which the reaction flask is open to air, N₂ should be flowing vigorously to create a protective blanket over the reagents in the flask. All N₂ used should be 99.9% or greater in purity.

1. Preparation of molecular precursors

1. Purification of ligand precursor

- NOTE: Myristic acid can be substituted by phenylacetic, oleic, or other long-chain carboxylic acids.
 - 1. Place a 100 mL 3-neck flask, a stir bar, a reflux condenser, a glass stopper, a thermowell, a T-adapter, and a hose adapter into a 160 °C oven overnight.
 - NOTE: Glassware can also be flame dried and placed in the oven for 1 h.
 - 2. Set up the flask, condenser, and thermowell on a Schlenk line while the glassware is still warm using high temperature vacuum grease to ensure glassware remains water-free. Close the final neck of the flask with a rubber septum.
 - Place 2.65 g of myristic acid (HO₂C₁₄H₂₇, 11.6 mmol) into the flask and flush with N₂. Put the flask under vacuum for 2 h with mild stirring at 120 °C to remove residual water from the acid.

2. Preparation of indium myristate $(In(O_2C_{14}H_{27})_3)$

NOTE: Equivalent InP clusters can be prepared with trimethylindium or indium acetate.

1 Preparation via trimethylindium (InMe₃)

- 1. Weigh out 0.512 g of InMe₃ (3.2 mmol, anhydrous) and dissolve it in 10 mL of anhydrous toluene. Draw the solution into a syringe and seal with a rubber septum to keep the solution air-free during removal from the glovebox.
- 2. Add 10 mL of anhydrous toluene to myristic acid from step 1.1 via a syringe and stir at room temperature until dissolved.
- Slowly add InMe₃ from step 1.2.1.1 via a syringe (~2 drops/s) while stirring. This step should result in rapid gas formation visible to the eye. Allow to stir for 10 min to ensure complete reaction.

2. Preparation via indium acetate (In(OAc)₃)

- 1. Weigh out 0.93 g of $In(OAc)_3$ (3.2 mmol) and add to the flask containing myristic acid from step 1.1 under positive N₂ flow.
- 2. Evacuate the flask and heat the flask to 100 °C while stirring. The mixture should melt. Let the solution off-gas acetic acid for 12 h (overnight) at 120 °C.
- 3. Refill the flask with N₂ and add 20 mL of anhydrous toluene via a syringe through the rubber septum.

2. Synthesis of In₃₇P₂₀(O₂CR)₅₁

- 1. Heat the reaction flask containing $In(O_2C_{14}H_{27})_3$ solution to 110 °C.
- Add 465 μL of P(SiMe₃)₃ (1.6 mmol) to 10 mL of anhydrous toluene in the glovebox. Draw the solution into a syringe and insert the needle into a rubber stopper until the needle opening is completely covered. Be cautious when removing from the glovebox as P(SiMe₃)₃ is a pyrophoric liquid.
- Rapidly inject the P(SiMe₃)₃ solution into the hot In(O₂C₁₄H₂₇)₃ solution. The solution should turn yellow quickly after the addition of P(SiMe₃)₃. Monitor the reaction by taking 50 μL aliquots of reaction solution into 3 mL of toluene for UV-Vis analysis. The reaction is finished when no further changes are seen in the aliquot spectra.
- 4. Remove from heat to cool the flask and halt the reaction.

NOTE: The growth of InP clusters is optimal at a temperature range of 100-110 °C. The reaction proceeds at lower temperatures, including room temperature, but goes very slowly. Higher temperatures result in evolution of quantum dots of varying sizes depending on the temperature. The reaction typically requires 20-60 min to go to completion, depending on the ligands used. Failure to run the reaction to completion could result in small, unstable clusters that will quickly decompose. Running the reaction past completion will not alter the cluster composition as long as the temperature is at or below 110 °C.

3. Workup of In₃₇P₂₀(O₂CR)₅₁

NOTE: All solvents used in the purification steps are anhydrous and stored over 4 Å sieves in the N₂-filled glovebox.

1. Isolation of In₃₇P₂₀(O₂CR)₅₁

- 1. Remove the solvent from the cluster solution under reduced pressure on the Schlenk line.
- 2. Seal the flask under N₂ using the glass stopper and T-adapter from the oven. Fasten the flask and adapters with electrical tape and bring into the glovebox.

2. Purification via precipitation, centrifugation, and re-dissolution

- 1. Resuspend the clusters in minimal toluene (~1 mL) and centrifuge to remove solid impurities (7,197 x g, 10 min). Decant and keep the clear, yellow supernatant and discard any solids.
- 2. Add 3 mL of acetonitrile (3:1, MeCN:tol) to the supernatant to precipitate the clusters (yellow precipitate) and centrifuge again under the same parameters. Discard the clear, colorless supernatant and resuspend the yellow solid pellet of clusters in minimal toluene.

3. Repeat step 3.2.2 for a total of 5 cycles.

3. Purification via column

- 1. Take the clusters dissolved in minimal toluene (~0.5 mL) and apply them in a thin band to a freshly cleaned size-exclusion, liquid column (60 cm, 25 mm) packed with permeable gel beads (see **Table of Materials**) using toluene as the solvent.
- Allow the clusters to run through the column ensuring to keep the beads wet by adding fresh toluene as the liquid runs through the column. Collect all yellow fluid but make sure to stop collecting immediately after the yellow passes as excess ligand will come off after the cluster. Typically, the clusters take about 20 min to elute at room temperature.
 NOTE: To confirm where the cluster region ends on the column, a laser pointer (405 nm) can be used to see where glowing resumes. The portion of the column containing clusters will not glow.
- Remove solvent under reduced pressure via a vacuum pump until a waxy solid is achieved. Store dry clusters under N₂ for best stability. In a typical synthesis, 1.2 g of clusters should be isolated, representing a 90% yield.

4. Synthesis of InP quantum dots using $In_{37}P_{20}(O_2CR)_{51}$ as a single source precursor

NOTE: Indium phosphide quantum dots can be synthesized from purified InP clusters using a heat-up or hot injection method.

1. Heat-up method

- 1. Degas a 100 mL 3-neck round bottom flask equipped with a stir bar, a glass thermowell, a T-adapter, and a rubber septum. Assemble the glassware using high temperature vacuum grease.
- Dissolve 200 mg of purified InP clusters in 20 mL of anhydrous 1-octadecene. Inject the InP cluster solution into the reaction flask via a syringe under a positive N₂ flow, followed by an additional 20 mL of anhydrous 1-octadecene. Briefly degas to ensure the reaction flask is air-free.
- 3. Heat the solution to 300 °C under a positive N₂ flow while stirring. The growth of QDs can be monitored by UV-Vis spectroscopy with timed aliquots. The bright yellow color persists up to around 200 °C and changes from yellow to bright orange to dark red-brown. The reaction is complete in 30-40 min.
- 4. Cool down the reaction flask to room temperature by removing the heating mantle. The solution after cooling displays an optically clear red color. Remove 1-octadecene by vacuum distillation at 160 °C. Replace the appropriate glassware as quickly as possible to limit air exposure.
- 5. Dissolve InP QDs using minimal amount (<5 mL) of anhydrous toluene in a N₂-filled glovebox. Transfer the crude solution to a centrifuge tube. Add ~40 mL of anhydrous acetonitrile and centrifuge for purification (7,197 x g, 10 min).
- 6. Pour off the supernatant and re-dissolve the precipitate in approximately 5 mL of anhydrous toluene. Repeat the purification steps for a total of 3 cycles. Store the purified product dissolved in anhydrous toluene.

2. Hot-injection method

- 1. Degas a 100 mL 3-neck round bottom flask equipped with a thermowell, a Schlenk adapter, and a rubber septum. Assemble the glassware using high temperature vacuum grease.
- 2. Inject 35 mL of anhydrous 1-octadecene into the reaction flask. Heat the solvent to 300 °C under inert gas while stirring.
- 3. Dissolve 200 mg of purified InP clusters in 5 mL of anhydrous 1-octadecene and inject the cluster solution into the reaction flask. The reaction is complete in 15-20 min.
- 4. Cool down the solution to room temperature by removing the heating mantle. Distill off 1-octadecene and purify InP QDs as described in steps 4.1.5 to 4.1.6.

5. Characterization of $In_{37}P_{20}(O_2CR)_{51}$ and InP quantum dots

1. Transmission electron microscopy (TEM)

- 1. Prepare a dilute solution of cluster (~5 mg) or quantum dots in pentane:toluene (1:1, 2 mL total). Solution color should be barely visible.
- Pick up a lacey carbon TEM grid (400 mesh, ultra-fine) with tweezers and place off the edge of a surface, making sure the grid is not touching anything besides the tweezers.
- 3. Drop-cast one large drop onto the grid and let it dry completely with no dabbing away solution (~20 min). Place the grid under vacuum and let further dry overnight.
- 4. Image the sample with TEM. Typical image conditions include spot size 5,200 kV electron beam, objective aperture completely open, and magnification of 350,000X.
- 5. In the native image format (.dm3), measure the particle size using the straight-line tool to create a line across the imaged particle (see Table of Materials for software). The command tool finder will give a length in nanometers corresponding to the drawn line, when the line is actively being dragged or clicked on and measure the particle diameter.

2. Nuclear magnetic resonance (NMR)

- NOTE: ¹H NMR needs as little as 20 mg of clusters, but ³¹P NMR requires at least 40 mg of clusters to resolve the cluster region.
 - 1. Prepare cluster solution (40 mg) in deuterated benzene (C_6D_6 , ~0.7 mL) in the glovebox and transfer the solution into an oven-dried Jyoung NMR tube. Seal the tube under N₂ and remove from the glovebox for measurements.
 - 2. Collect ¹H NMR spectra on a 300 MHz or greater instrument. Common parameters include 2 dummy scans, 6 scans, and 30 s delay time.
 - Collect ³¹P NMR spectra on a 500 MHz or greater instrument. Use a phosphoric acid standard to calibrate the instrument prior to use. Common parameters include an offset of -100 ppm, sweep width of 500 ppm, and 256 scans repeated 40 times (about 14 h of total run time to ensure a strong enough signal).

3. X-ray Diffraction (XRD)

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- 1. Prepare a highly concentrated solution of clusters or quantum dots by either dissolving dried material in minimal toluene (< 1 mL) or removing toluene from a stock solution.
- Drop-cast onto an oven-dried Si wafer and let dry for ~30 min. For consistency of drop size, use a digital micropipette with the setting at 3~5 µL. Repeat 2-3 times until a film of clusters or quantum dots has sufficiently set.
- 3. Collect XRD data from 10 to 70° with 5.5° intervals. Set each interval to 30 s acquisition time for a quick run or 240 s acquisition for higher resolution.

4. Photoluminescence (PL)

- 1. Transfer the solution for PL analysis into a 1 x 1 cm quartz fluorescence spectrophotometer cell.
- 2. Set the excitation at 450 nm and the monochromator slit widths for both entrance and exit slits at 3 nm. Set the integration time at 0.1 s/ nm or 1 s/nm for higher resolution.

Representative Results

InP clusters and quantum dots are characterized by UV-Vis absorption and PL spectroscopy, XRD, TEM, and NMR spectroscopy. For the InP clusters, an asymmetric absorption feature is observed, with a peak maximum at 386 nm (**Figure 1a**). Despite the true monodispersity of the sample, this lowest energy peak exhibits a broad linewidth, which narrows upon decrease in temperature. This has been attributed to a set of discrete electronic transitions that are specific to the vibrational motions of the low-symmetry nanocluster lattice¹⁷. No appreciable PL QY is observed for clusters at 298 K despite the lack of obvious trap states that would arise from undercoordinated indium or phosphorus ions.

The non-stoichiometric, In-rich cluster (where In is present in a 1.85:1 ratio relative to phosphorus) results in a structure that corresponds with neither the zinc blende nor the wurzite XRD patterns of bulk InP (**Figure 1b**). Instead, the InP clusters attain a low-symmetry, pseudo- C_{2v} structure that is best described by a set of intersecting polytwistane units²⁵. The core diameter is in the 1-2 nm range depending on the axis from which it is viewed (**Figure 1c**). This low symmetry structure is reflected in the solution-phase ³¹P NMR spectrum of the cluster. The ³¹P NMR spectrum of myristate-capped InP clusters shows 11 distinct peaks (2 P atoms on the C₂ axis that each give a unique peak and the remaining 18 P each have a symmetry equivalent, resulting in an additional 9 peaks) ranging from -187 to -242 ppm (**Figure 1d**)²⁶. The broadness observed in the ³¹P NMR spectrum varies as a function of solvent and concentration, and purification method as has been recently described for related nanoscale systems²⁷.

The optical spectra of InP QDs synthesized from clusters using the method described here display a lowest energy excitonic transition (LEET) at 564 nm and the corresponding PL emission peak at 598 nm with a full width at half maximum of 52 nm and trap emission evident at redder wavelengths (**Figure 2a**). It is worth noting that while the two synthetic methods (heat-up and hot-injection) yield InP QDs of comparable optical quality, the hot injection method typically leads to a sample with higher monodispersity due to the rapid nucleation at elevated temperature¹³. The typically low PL quantum yields obtained directly from the synthesis without further surface treatment (shelling, F- etching, or Lewis acid coordination) are hypothesized to result from a mixture of hole and electron traps present at the surface of these nanocrystals^{18,28}. The XRD pattern of the resultant InP QDs confirms the zinc blende phase (**Figure 2b**). Peak broadening in the XRD data occurs due to the finite size of the highly crystalline structures, which in the case of InP QDs is 3.1 nm +/- 0.5 nm in diameter (**Figure 2c**, a size histogram can be found in ref. 13).



Figure 1. Representative characterization data for InP clusters. (A) UV-Vis spectrum of InP clusters. (B) XRD pattern for purified InP clusters showing deviation from the expected bulk zinc blende (black trace) and wurtzite (grey trace) InP pattern. (C) TEM image of isolated InP clusters. (D) 31 P NMR spectrum of InP clusters collected at 202 MHz in C₆D₆ at 298 K. Please click here to view a larger version of this figure.





Figure 2. Representative characterization data for InP quantum dots prepared from InP clusters. (A) UV-Vis (solid) and PL (dotted) spectra of InP QDs prepared from myristate-capped InP clusters using the hot-injection protocol. (B) XRD pattern of purified InP QDs showing agreement with the bulk zinc blende InP pattern. (C) TEM images of InP QDs grown from clusters using the hot-injection protocol. Please click here to view a larger version of this figure.

Discussion

The synthesis of InP magic-sized clusters and their conversion into quantum dots follow straightforward procedures that have been shown to consistently produce high quality samples. The ability to synthesize and isolate InP clusters as an intermediate has distinct advantages in terms of subjecting these nanostructures to modifications that can be well-characterized and consequently be incorporated in the final QDs. The atomically precise nature of the clusters and the high reproducibility provide a platform for innovative studies in surface modifications, defects, and alloying of the InP systems and open doors to a wide range of applications such as in displays, solid-state lighting, catalysis, and photovoltaics.

In the synthesis of InP clusters, it is critical that all reagents are of high purity and thoroughly dried, as the success of the synthesis is contingent upon water- and air-free experimental conditions and purity of the precursors for uniform growth in high yields. Additionally, it is recommended that sufficient precautions are taken when handling $P(SiMe_3)_3$, which is light-sensitive and pyrophoric. This reagent should be stored in a light-, air-, and water-free environment and caution should be taken to prevent air and water exposure before and during the reaction. For efficient growth of the clusters, the temperature range should be 100-110 °C; at room temperature, the growth is extremely slow, and a higher temperature will result in conversion into quantum dots of varying sizes depending on the temperature. The presented protocol is also highly scalable and versatile, allowing synthetic control and modifications through a breadth of parameters. The myristic acid used as the ligands for InP clusters and subsequent QDs can be replaced by phenylacetic acid, oleic acid, or other short and long-chain carboxylic acids. Post-synthetic addition of $P(SiMe_3)_3$ to solutions of InP clusters that have slightly perturbed absorption features (red-shifted and/or broadened) has been observed to result in a size focusing effect where the consumption of excess indium myristate results in a ~3 nm blueshift in the absorption spectra²⁹.

The purification method of the clusters has been empirically optimized in our lab to avoid oxidation and to isolate the highest possible yields. The choice of acetonitrile as the antisolvent and its volume ratio with toluene fulfill these goals. Finally, the clusters are resuspended in minimal amount of toluene and centrifuged to remove any solid impurities that may have resulted during synthesis. Removing toluene from the final solution gives a yellow paste that can be stored for at least 36 months under air- and water-free conditions. It should also be noted in regard to preparing NMR samples for characterization of the purified product that the precise chemical shifts for the 11 distinct resonances in ³¹P NMR spectrum vary depending on the identity of the indium precursors. Furthermore, insufficient purification and variation in cluster concentration can result in line broadening. In order to obtain a clean spectrum with sharp features, it is suggested that at least 40 mg of the cluster is dissolved in a minimal amount of anhydrous C_6D_6 (~0.7 mL).

Similarly, the synthesis of InP QDs via clusters must be performed under water- and air-free conditions. Previous studies have shown that the presence of water in indium precursors and the addition of trace amounts of water or hydroxide lead to significant changes in the growth of InP QDs and the surface chemistry of the final product²⁵. When running the reaction at a different scale than described in the protocol, it should be noted that for the hot-inject method, the cluster solution for injection should be sufficiently concentrated and the volume should be smaller compared to the heated solvent in the flask. This is to minimize the abrupt decrease in temperature as the reaction temperature profile plays a nontrivial role in the synthesis. Detailed work on the conversion mechanism of InP clusters to QDs has been recently reported where the effects of the addition of different precursors (i.e., carboxylic acid, indium carboxylate), temperatures, and concentration have been explored³⁰. Through these studies, it has been revealed that thermolysis temperatures > 220 °C are required for obtaining high yields of optimal quality QDs. The purification of InP QDs follows similar logic and process as mentioned above for the clusters, except that the storage of purified QDs is recommended in solution with a solvent such as toluene. In solid form, the QDs have been observed to form aggregates over time, preventing homogeneous colloidal dispersion. One final note regarding the protocol is that removing 1-octadecene by vacuum distillation after the synthesis of InP QDs rather than by only precipitation-redissolution is a recommended first step of QD purification. This is to limit the volume of solvent required in the workup and because the residual ODE may interdigitate with the long-chain carboxylate ligand shell, causing difficulties with sample preparation for characterization and subsequent use.

We have demonstrated the synthesis and characterization of atomically-precise InP magic-size clusters, $In_{37}P_{20}(O_2CR)_{51}$, and their use as single source precursors for the synthesis of InP quantum dots using both heat-up and hot-injection methods. The reported synthesis of InP clusters is versatile and can be generalized to a wide range of alkyl carboxylate ligands. The synthesis of the InP QDs from the clusters provides a highly reproducible method for the synthesis of these challenging nanostructures with high quality in terms of size distribution and crystallinity. Opportunities abound for further elaboration of this method through post-synthetic modification of the clusters themselves and for engineering the cluster to quantum dot conversion strategy. Because of this, we believe these methods are useful and potentially technologically meaningful for the synthesis of InP and related emissive materials for display and lighting applications.

Disclosures

The authors have nothing to disclose.

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