Monodispersed InP Quantum Dots Prepared by Colloidal Chemistry in a Noncoordinating Solvent

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III–V semiconductor quantum dots are of considerable interest as their applications cover a broad spectrum, from optoelectronic to biomedical technology. For them to be of practical value, there is a need for a method that provides rapid and scalable production of highly monodispersed nanoparticles. This paper reports an efficient and rapid method of producing highly monodispersed InP quantum dots using a novel precursor-based colloidal synthesis in a noncoordinating solvent. The method also allows judicious control over the size of the quantum dots and can also be extended to produce other III–V quantum dots. In this paper, the synthesis and characterization of highly monodispersed InP quantum dots from newly prepared indium(III) carboxylate complexes in octadecene are detailed. When using indium(III) carboxylate as the indium precursor, no surfactant or coordinating solvents are required to prepare high-quality InP quantum dots in octadecene. The in situ formation of a surfactant upon injection of the phosphine precursor [P(SiMe3)3] helps control the growth of the resulting quantum dots. Structural and optical studies (continuous wave and time-resolved) have been performed on the as-prepared InP quantum dots. In addition, time-resolved photoluminescence has been conducted on etched InP quantum dots. The effects of the carboxylate chain length in indium(III) carboxylate and injection temperature on quantum dots. In addition, time-resolved photoluminescence has been conducted on etched InP quantum dots. The effects of the carboxylate chain length in indium(III) carboxylate and injection temperature on the growth and properties of quantum dots have been studied.

Introduction

The synthesis of III–V semiconductor nanocrystals has been an area of intense research over the past 20 years. Since Wells et al. first demonstrated the dehalosilylation reaction in the synthesis of InAs and GaAs, many other groups have spent considerable time and effort on solution phase synthesis of III–V semiconductor nanoparticles. The principal interest in semiconductor nanoparticles [or quantum dots (QDs)] lies in their optical properties which are dramatically affected by quantum confinement. Since QD physical dimensions are comparable to the carrier de Broglie wave function in semiconductors, energy states of the electrons and holes are quantized. As a result, the emission efficiencies of semiconductor QDs are substantially higher than those of their bulk counterparts, and most importantly, the emission wavelength varies as a function of dot size. These properties

make colloidal dots, readily dispersible in a host medium, very attractive for optical device applications such as hybrid light-emitting diodes, photorefractive devices, and potential laser development. Furthermore, the “dark” (optically forbidden) character of the lowest exciton state and the long carrier lifetimes measured in colloidal dots are characteristics which make QDs good candidates for spintronics and quantum computing applications.

The main advantages offered by III-V semiconductor nanocrystals (as opposed to the II-VI QDs which are already commercially available) lie in the robustness of the covalent bond in III-V semiconductors versus the ionic bond in the II-VI semiconductors and in the reduced toxicity of compounds such as InP. This makes III-V quantum dots (e.g., InP) a potentially better candidate than II-VI quantum dots (e.g., CdSe) for biological applications such as bioimaging or photodynamic therapy.

This work reports the synthesis of high-purity indium(III) carboxylate precursors, where the carboxylate is myristate, stearate, and laurate, via direct elimination of cyclopentadiene. These high-purity indium(III) carboxylate precursors have enabled us to report the first nanoparticle preparation of InP(III) myristate, and indium(III) stearate, and laurate, via direct elimination of cyclopentadiene precursors, where the carboxylate is myristate, stearate, and laurate, via direct elimination of cyclopentadiene.

Elemental Analysis. The elemental analyses reported here were conducted by Prevalere Life Sciences, Inc. (Whitesboro, NY). For all samples, only the percentages of carbon and hydrogen were analyzed. Anal. Calcld for indium(III) laurate (C_{36}H_{69}InO_{6}): C, 63.30; H, 10.25. Found: C, 61.91; H, 9.98. Anal. Calcld for indium(III) stearate (C_{42}H_{81}InO_{6}): C, 63.64; H, 10.96. Found: C, 66.21; H, 11.19. For comparison. Anal. Calcld for myristic acid (C_{15}H_{30}O_{2}): C, 71.95; H, 12.08. Found: C, 71.52; H, 12.50. For comparison. Anal. Calcld for myristic acid (C_{15}H_{30}O_{2}): C, 73.63; H, 12.36. Found: C, 73.78; H, 13.82. For comparison. Anal. Calcld for stearic acid (C_{17}H_{34}O_{2}): C, 76.00; H, 12.76. Found: C, 75.76; H, 12.47.

NMR Spectroscopy. The 1H NMR spectra were recorded at 400 MHz by using a Varian XL 400 spectrophotometer. All air-sensitive samples for the NMR spectra were contained in flame-sealed NMR tubes. Chemical shifts are reported in δ (parts per million) and are referenced to tetramethylsilane (TMS) as δ = 0.00 ppm and benzene as δ = 7.15 ppm. All of the indium(III) carboxylates are only slightly soluble in hot benzene, so throughout the analyses of the various complexes, the reported temperatures are the temperatures at which the spectra were collected.

Indium(III) laurate: 1H NMR (d_{6}-benzene, 55 °C) δ 2.59 (br, 2H), 1.78 (quintet, J = 7.0 Hz, 2H), 1.32 (br, 16H), 0.924 (triplet, J = 6.2 Hz, 3H); 1H NMR of lauric acid (d_{6}-benzene, RT) δ 12.72 (br, 1H), 2.08 (triplet, J = 7.6 Hz, 2H), 1.47 (quintet, J = 7.0 Hz, 2H), 1.25–1.13 (br-m, 14H), 0.91 (triplet, J = 6.8 Hz, 3H).

Indium(III) myristate: 1H NMR (d_{6}-benzene, 45 °C) δ 2.55 (triplet, J = 7.20 Hz, 2H), 1.76 (quintet, J = 7.2 Hz, 2H), 1.33 (br, 20H), 0.92 (triplet, J = 6.8 Hz, 3H); 1H NMR of myricityl acid (d_{6}-benzene, RT) δ 12.57 (br, 1H), 2.08 (triplet, J = 7.4 Hz, 2H), 1.47 (quintet, J = 7.2 Hz, 2H), 1.29–1.13 (br-m, 10H), 0.91 (triplet, J = 7.0 Hz, 3H).

Indium(III) stearate: 1H NMR (d_{6}-benzene, 55 °C) δ 2.42 (br, 2H), 1.72 (br, 2H), 1.35 (br, 28H), δ 0.91 (br, 3H); 1H NMR of stearic acid (d_{6}-benzene, RT) δ 12.38 (br, 1H), 2.07 (triplet, J = 7.6 Hz, 2H), 1.47 (quintet, J = 6.8 Hz, 2H), 1.33–1.14 (br-m, 28H), 0.91 (triplet, J = 7.0 Hz, 3H).

Synthesis of InP Nanocrystals. Within the glovebox, the reaction vessel was loaded with a stir bar and the indium precursor was as follows: 63.2, 58.3, and 88.53% for indium(III) laurate, indium(III) myristate, and indium(III) stearate, respectively.

Experimental Section

Synthesis. In(C_{6}H_{12})_{3} was prepared according to the literature method. Tris(trimethylsilyl)phosphine [P(TMS)_{3}], myristic acid, stearic acid, lauric acid, and technical grade (90%) 1-octadecene (ODE) were purchased from Aldrich Chemical Co. All solvents were carefully dried by using conventional procedures. All compounds described in this investigation were treated as if they were commercially available, except for the indium precursor, which was carefully dried by using conventional procedures. All compounds described in this investigation were treated as if they were commercially available, except for the indium precursor, which was carefully dried by using conventional procedures.
(approximately 500 µmol). Also within the glovebox, approximately 250 µmol of P(TMS)₃ was loaded into a four-dram vial containing ~4 mL of dry ODE and capped with a rubber septa. After removal from the glovebox, the reaction vessel was placed in a 500 mL round-bottom heating mantle which was filled with sand. Then the reaction vessel was connected to a Schlenk line, and with an argon flow, 40 mL of ODE was added via a syringe. Next, with the stirrer going, the temperature was set to 100 °C and the reaction vessel was placed under vacuum for at least 1 h. Then the vessel containing a colorless optically clear solution was backfilled with Ar(g), and the temperature was set to the desired reaction temperature (250–300 °C). Once the reaction temperature was reached, the phosphine solution was rapidly injected via a 10 mL syringe. After a desired period of time, usually 1 or 10 min, an additional 40 mL of ODE was added and the temperature set to the growth temperature (200–250 °C). Throughout the reaction, the solution gradually changed color from clear and colorless to transparent yellow-orange, then transparent orange, then transparent light red, then transparent bright red, then transparent dark red, and sometimes a dark brown almost black color. The rate and extent of color change depended on the reaction temperature and time. Aliquots of the reaction mixture (0.5 mL in approximately 5 mL of chloroform or hexanes) were taken at various times (typically 1, 2.5, 5, 10, 15, 30, and 45 min and 1, 1.5, and 2 h) to follow the growth process. Most reactions were stopped after 2 h by removing the mixtures from the heat source and allowing gradual cooling to room temperature. For structural characterization, the final products of these reactions were isolated by the addition of a 4–5-fold excess of acetone to the reaction volume of ODE. Centrifugation of this mixture at 11 000 rpm for 20 min at 20 °C produced the crude product. Later it was discovered that dilution of the crude product after the initial precipitation in chloroform, followed by precipitation with acetone, led to precipitation of two different species: the InP(QDs) which are more dense than the solvent and another solid that was less dense than the solvent. Repeated washing and removal of the precipitate on top leads to the isolation of purer InP(QDs). Synthesis of InP Nanocrystals for Temperature Study and Carboxylic Chain Length Study. Within the glovebox, the reaction vessel was loaded with a stir bar and the indium(III) carboxylate precursor (approximately 250 µmol). Also within the glovebox, approximately 125 µmol of P(TMS)₃ was loaded into a four-dram vial containing ~4 mL of octadecene and capped with a rubber septum. Following the same procedures described above, the phosphine precursor was injected to start the reaction. For this temperature dependence study, the initial temperature was maintained throughout the course of the reaction. Aliquots of the reaction mixture (0.25 mL in approximately 5 mL of chloroform) were taken at various times (30 s, 1, 2.5, 5, 10, 15, 30, and 45 min, and 1, 1.5, and 2 h) to follow the growth process. The final products of these reactions were not processed further.

Characterization of InP(QDs). The resulting nanoparticles were characterized by UV–vis spectroscopy, photoluminescence (PL) spectroscopy, photoluminescence excitation (PLE) spectroscopy, transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) spectroscopy.

UV–Visible Absorbance. The absorbance spectra were measured by using a Shimadzu model 3101PC UV–vis–NIR scanning spectrophotometer or a Hewlett-Packard 8452A diode array spectrophotometer with the samples in 1 cm cuvettes.

Transmission Electron Microscopy (TEM) and Electron Diffraction (ED). Transmission electron microscopy (TEM) and electron diffraction (ED) images were obtained with a model 200 JEOL microscope at an acceleration voltage of 200 kV. Some specimens were prepared by drop casting the toluene/hexane dispersion onto an amorphous carbon-coated 300 mesh copper grid. Other specimens were prepared by drop casting chloroform dispersions onto an amorphous carbon-coated 300 or 200 mesh copper grid. Selected area electron diffraction was assessed at a camera length of 60 cm.

X-ray Photoelectron Spectroscopy (XPS). XPS studies were performed on a Physical Electronics/PHI 5300 X-ray photoelectron spectrometer with a hemispherical analyzer and a single-channel detector, operated at 300 W (15 kV and 20 mA). Mg Kα radiation (1253.6 eV) and pass energies of 89.45 eV for survey scans and 17.9 eV for high-resolution scans were used. Three samples were analyzed: indium(III) stearate, unwashed InP(QDs), and pyridine-washed InP(QDs). Indium(III) stearate, prepared as described above, was used without any further purification. The unwashed InP/In₂O₃(QDs) were prepared as described above by treating 500 µmol of In(steareate)₃ in 40 mL of 240 °C ODE with 250 µmol of P(TMS)₃. Upon completion of the reaction, the particles were isolated by precipitating with acetone and centrifugation. The unwashed QDs were then combined into one centrifuge tube from six tubes by addition of chloroform followed by precipitation with methanol. After centrifugation and decantation, the QDs were placed under vacuum at RT for ~2 h and then submitted for XPS analysis. The pyridine-washed InP(QDs) were prepared by taking a sample of unwashed QDs and stirring it in 25–30 mL of pyridine overnight (~16 h). The QDs then were precipitated by hexane addition and centrifugation. These particles were then placed under vacuum at room temperature for ~2 h and submitted for XPS analysis. These samples were mounted by placing the powder samples directly onto sticky tape that is directly connected to the Au puck.

Energy Dispersive X-ray Spectroscopy (EDAX). EDAX was obtained with a Hitachi S-4000 field emission scanning electron microscope. The microscope operated at an electron acceleration voltage of 20 kV. The sample was cast as a thin film from the dispersion or simply used as a powder on a silicon or graphite substrate. The X-ray fluorescence beams were collected with an X-ray collection unit IXRF 500 system. Quantitative estimates of elements were made by comparing the spectra against that of a corresponding commercial standard InP crystal. The sample measured was the sample described directly above as the pyridine-washed sample.

X-ray Diffraction (XRD). X-ray diffraction spectra were recorded on a Siemens D500 spectrometer using the Cu Kα radiation. A powder of the sample, obtained by precipitating the product at the end of the reaction with acetone, was placed on a glass slide, and the scanning angle was slowly varied by rotating sample geometry. The 2θ angles that were probed were from 3° to 60° scanned at a rate of 2°/min.

Photoluminescence (PL) and Photoluminescence Excitation (PLE) Spectroscopy. Continuous wave (CW) PL and PLE spectra were acquired in the frontal geometry using a Jobin Yvon Fluorolog-3 spectrophluorometer equipped with a 400 W Xe lamp as the excitation source and a Hamamatsu R928 photomultiplier (PMT) tube as the detector. All spectra were corrected for the PMT response and/or the lamp emission spectrum. The emission of aliquots taken directly from the reaction mixtures as described in the synthesis section were collected from solutions in quartz cuvettes.

Time-Resolved Photoluminescence (TRPL) Spectroscopy. The time-resolved photoluminescence (TRPL) measurements were performed in the right angle geometry using 400 nm, 200 fs pulses with a repetition rate of 250 kHz, obtained by frequency doubling the 800 nm pulsed output of a Coherent Rega 9000 regenerative amplifier. The PL spectra were spectrally and temporally resolved.
using a 250IS Chromex monochromator (spectral resolution of 0.15
nm) equipped with a Hamamatsu C4334 streak camera with a
traditional jitter of 50 ps. All time-resolved measurements were
carried out at room temperature, with the samples placed in the same 1
cm optical path quartz cuvettes used for the CW studies.

Results and Discussion

Preparation of Indium Precursors. The direct metha-
thetical reaction between InCl₃ and a sodium or lithium salt
of the corresponding carboxylic acid would be the least
expensive pathway for the preparation of these types of
precursors. In our preliminary attempts to prepare In-
(carboxylate)₃ directly utilizing a metathetical reaction (eq
1), a complex mixture of products was isolated in which
halide free In(carboxylate)₃ could not be isolated even after
Soxhlet extraction of the crude product with toluene.

InCl₃ + 3NaOC(O)(CH₂)nCH₃ \xrightarrow{\text{solvent temperature}} In[OC(O)(CH₂)nCH₃]₃ + 3NaCl (1)

Since the direct metathesis reaction did not result in the
isolation of pure In(carboxylate)₃ compounds, an elimination
pathway was attempted directly from In(C₅H₅)₃ and the
corresponding carboxylic acid (eq 2).

In(C₅H₅)₃ + 3HOC(O)(CH₂)nCH₃ \xrightarrow{\text{RT}} In[OC(O)(CH₂)nCH₃]₃ + 3HC₅H₅ (2)

We discovered that this elimination reaction proceeds at
room temperature within 4 h to yield the corresponding indium(III) carboxylate complexes. As detailed in the
Experimental Section, all of these compounds were charac-
terized by ¹H NMR spectroscopy and elemental analysis.
These compounds are slightly soluble in benzene at elevated
temperatures. On the basis of the NMR spectroscopy results,
only one indium(III) carboxylate species is present at the
collection temperature with all the carboxylate ligands being
shifted downfield compared to those of the acids:

\begin{align*}
\text{In(III) laurate} & : \delta = 2.59, 2.55, 2.42 \\
\text{In(III) myristate} & : \delta = 2.08, 2.08, 2.07 \\
\text{In(III) stearate} & : \delta = 1.78, 1.76, 1.72
\end{align*}

All the remaining hydrogens are not significantly affected
by indium, relative to the corresponding acids.

The experimentally determined elemental analyses are in
good agreement with the calculated values (Table 1). The
largest variation is seen in the percent hydrogen of indium-
(III) myristate, which was off by 0.27%. This corresponds
to a percent error of 2.63% which is within the 5% error
limits of the analysis technique.

Spectral Monitoring of in Situ Growth. With the
successful synthesis of pure indium(III) carboxylate com-
plexes, we undertook the synthesis of InP(QDs) as described
above. This synthesis is a fast process in which nucleation
is immediate after injection and the growth step can be
controlled by varying the growth temperature. By taking
advantage of the fast nucleation and slow growth, we
prepared relatively monodispersed crops of InP(QDs).

Since we can control the nucleation and growth steps
utilizing this fast reaction which does not utilize any
surfactants, or coordinating ligands that, in some cases can,
obscurce the optical properties of the as-grown QDs, we
are able to follow the reaction progress by in situ monitoring of
the absorbance, photoluminescence, and photolumines-
cence emission spectra. Figure 1 displays typical UV—vis and PL spectra that are obtained from aliquots taken directly
from a reaction mixture. These aliquots are an example of
the reaction mixture, as upon injection of the hot reaction
mixture into the cool room-temperature solvents the growth
should be quenched. The exact reaction parameters for the
reaction used to generate Figure 1 involved injection of the
phosphine precursor [P(TMS)₃] at 300 °C, followed by a
rapid injection of 40 mL of ODE to rapidly cool the reaction
mixture to the growth temperature of 245 °C. As can be seen
in Figure 1A, there is a strong absorption feature after 5 min,
with an absorption maximum at approximately 499 nm,
which undergoes a red shift over time, at the growth
temperature, to approximately 549 nm after 3 h. The full
width at half-maximum (fwhm) of the absorbance feature
is 68 nm after 5 min and grows to only 72 nm by the end of
the reaction (3 h), indicating that there is control over the
population of particles throughout the reaction.

The photoluminescence (PL) studies performed on these
samples are shown in Figure 1. The photoluminescence was
excited using wavelengths considerably shorter than the
absorption edge of the nanocrystals (350 or 400 nm),
allowing us to record the ensemble PL spectrum (or “global”

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Table 1. Elemental Analysis Results for Indium(III) Carboxylates

<table>
<thead>
<tr>
<th>carboxylate</th>
<th>calc % composition</th>
<th>experimental % composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>carbon</td>
<td>hydrogen</td>
</tr>
<tr>
<td>laurate</td>
<td>60.66</td>
<td>9.76</td>
</tr>
<tr>
<td>myristate</td>
<td>63.30</td>
<td>10.25</td>
</tr>
<tr>
<td>stearate</td>
<td>67.19</td>
<td>10.96</td>
</tr>
</tbody>
</table>

Figure 1. Typical absorption and emission spectra of InP(QDs).
PL), which contains contributions from all nanocrystal sizes. For these specific reaction conditions, the PL spectrum of the “as-grown” solution contains a fairly sharp feature (60 nm fwhm after 5 min to 64 nm fwhm after reaction completion) red shifted by 46–55 nm, depending on time, with respect to the absorption edge of the nanocrystals. There is an accompanying much broader feature, on the long wavelength side of the spectrum, extending all the way into the IR region. In many cases, the broad feature dominated the spectrum. PLE spectra of the 5 min sample (Supporting Information), measured at emission wavelengths associated with the peak of the sharp PL feature (554 nm), exhibit a peak at an energy corresponding to the absorption edge of the InP nanocrystals. The sharp PL feature corresponds to the radiative recombination inside the InP nanocrystals. The origin of the broad feature (710 nm) is also related to the nanocrystals, since the PLE spectrum recorded at this wavelength is almost identical to the one associated with the sharp feature, as shown in the Supporting Information. On the basis of these observations, the sharp feature is assigned to band edge recombination in the nanocrystals and the broad feature is associated with recombination involving surface or defect-related states. It is interesting to note that the sharp feature associated with band edge recombination is already present in the PL spectrum of the reaction mixture, 5 min after the reaction has begun. As the growth progresses, the band edge:surface state emission intensity ratio increases in favor of the former, and the entire spectrum shifts toward longer wavelengths, indicating that the nanocrystals become larger. The PL data are similar to results2–6 reported for InP nanocrystals grown through the traditional method, with one significant difference: in all cases of the latter, a post-growth size selective precipitation must be performed on the original product to observe the sharp feature associated with band edge recombination. This is an indication that the size distributions obtained through the growth process we adopt here are comparable to the ones in previous reports, only after size-selective precipitation through the traditional methods. The emission efficiency of the as-grown nanocrystals varies from 0.5 to 2% from sample to sample. These reduced numbers can be explained by assuming insufficient surface passivation of the nanocrystals and the presence of nonradiative traps, generated by indium dangling bonds on the nanocrystal surface, as studied and discussed in detail by Fu and Zunger.10

**Structural Characterization of Quantum Dots.** A high-resolution transmission electron microscopy (HRTEM) image and a selected area electron diffraction (ED) image of a typical reaction product have been captured (Figures 2 and 3, respectively). The injection temperature for this specific reaction was 260 °C; after 10 min, ODE was added and the growth temperature was set to 200 °C. After isolation of the particles and three successive dissolutions (in CHCl₃), followed by precipitation with methanol, the entire sample (dissolved in ~20 mL of CHCl₃) was placed in a dialysis membrane (Spectra/Por 6–8000 MWCO) and dialyzed for 24 h, with the CHCl₃ being changed twice. From the resulting HRTEM images (Figure 2), we can discern lattice fringes and detect crystalline InP(QDs). On the basis of the TEM of this sample, we were able to obtain an average size of 3.05 ± 0.32 nm (standard percent deviation of 10.5%) of particles based on a total of 85 particles.

The ED patterns (Figure 3) consist of discrete rings depicting the crystalline nature of the particles. The diameters of the rings are consistent with the zinc blende phase of InP. The expected ratio of the 111, 200, 220, 311, and 222 rings is 1:1.16:1.48:1.89:2.01, which agrees well with our experimental ratio of 1:1.16:1.48:1.89:2.01.

Typical X-ray diffraction (XRD) spectra of both unwashed and washed samples are shown in Figure 4. The InP(QDs) used for the XRD were synthesized by injecting the phosphine at 300 °C, adding ODE after 1 min, and setting the growth temperature to 200 °C. The diffractogram agrees with the bulk zinc blende structure. The diffraction peaks for lattice
planes (111), (220), and (311) are found at 2θ values of 26.6°, 44.4°, and 52.5°, respectively. The indexing gives a bulk lattice parameter of 5.9 Å. There is an extra peak at the 2θ value of 21.4° in the unwashed sample which originates from the unreacted indium myristate associated with the nanocrystals. Using the Scherrer formula 

\[ d_{\text{domain}} = \frac{0.9\lambda}{\beta \cos \theta} \]

where \( \lambda \) is the wavelength of the X-ray and \( \beta \) is the full width at half-maximum (fwhm) of the diffraction peak at angle \( \theta \), the average domain size \( d_{\text{domain}} \) is found to be \( \approx 2.86 \) nm. This closely agrees with the size statistics revealed by the TEM image.

X-ray photoelectron spectroscopy (XPS) was used to determine the elemental composition of indium(III) stearate, unwashed InP(QDs), and pyridine-washed InP(QDs) (Figures 5 and 6). The survey spectra of each sample is shown in Figure 5. The survey spectra indicate the presence of indium, phosphorus, carbon, and oxygen. The presence of indium, carbon, and oxygen is easily observed in the survey spectra; however, high-resolution XPS (HR-XPS) analysis was required to observe the P 2p binding energies. Figure 6A depicts the high-resolution spectra of the P 2p region. In the two InP(QDs) samples, the presence of two peaks at \( \approx 133 \) and \( \approx 129 \) eV is obvious. Very similar binding energies have been previously reported for InP(QDs) prepared by the traditional TOPO method. Guzelian et al. reported that the P 2p peak positions of the TOPO-coated InP(QDs) were centered at 129.2 ± 0.2 and 133.4 ± 0.14 eV, which corresponded to phosphorus from InP and oxidized phosphine, respectively. In Figure 6B, the HR-XPS spectra of the indium binding energies are displayed. The indium core is orbit split to 3d\(_{3/2}\) and 3d\(_{5/2}\), with the 3d\(_{3/2}\) peak positioned at 446 eV and the 3d\(_{5/2}\) peak positioned at 453 eV. Guzelian et al. found that the In 3d\(_{3/2}\) peak varied from 444.7 to 445.6 eV.

The XPS and HR-XPS spectra show that, regardless of the sample that was analyzed, the binding energies of the indium, phosphorus, oxygen, and carbon are very similar from sample to sample, with the largest shift being 0.3 eV. When the In 3d\(_{5/2}\) peak binding energy of the indium precursor is compared to that of the pyridine-washed sample, there is an only 0.3 eV shift. On the basis of this study, XPS only indicates the presence of InP without providing a qualitative measure of the purity of the samples that were analyzed.

**Steady State Spectroscopy of Etched Quantum Dots.** To determine if the as-grown InP(QDs) were comparable in quality to the samples prepared utilizing the traditional synthesis approach, we treated our InP(QDs) with an HF etching process, very similar to those reported in the literature. The PL spectra of three different samples are presented in Figure 7. The emission efficiencies are as high as 20% at room temperature, and the broad feature associated with the unpassivated indium dangling bond is almost entirely eliminated, confirming that its presence in the as-grown nanocrystal PL spectra is related to surface states. These efficiencies are comparable to the ones reported in the literature for InP(QDs).

**Time-Resolved Spectroscopy of Etched Quantum Dots.** We performed time-resolved photoluminescence spectroscopy on the same samples in solution at room temperature to gain more information about carrier lifetimes and the nature of the radiative recombination. The PL intensity decay as a function of time is plotted in Figure 8 for several wavelengths across the PL profile. The decay has a multi-
measured in InP nanocrystals grown through the traditional method.2 The recombination lifetimes are long (tens of nanoseconds) in comparison with typical decay times measured in bulk semiconductors. A possible explanation for the elongated lifetimes lies in the dark dipole-forbidden nature of the lowest excitonic state. Theoretical studies predict that in semiconductor nanocrystals, the electron–hole exchange interaction lifts the 8-fold degeneracy of the band edge exciton, and the result is that the lowest-energy exciton state is an optically forbidden state. The energy splitting between the forbidden lowest-energy exciton state and the first optically allowed exciton state takes values ranging between the forbidden lowest-energy exciton state and the first allowed state and the excitons subsequently relax through a radiative process.

In this framework, the absorption takes place on the optically allowed exciton state takes values ranging between the forbidden lowest-energy exciton state and the first allowed state and the excitons subsequently relax through a radiative process. This PL with respect to the absorption edge as discussed earlier. The red shift we measure in the ensemble PL experiments reported here does not represent the exact allowed to forbidden (resonant) shift; fluorescence line narrowing measurements will be performed in the future to establish the magnitude of the shift. To conclude our discussion on the results of the preliminary optical measurements, we emphasize that, despite being grown through a different approach, our InP nanocrystals exhibit optical properties which are remarkably similar to the ones measured for nanocrystals grown through a traditional method.3–14 This study offers the possibility of establishing the influence of surfactants and/or growth parameters on the optical properties and isolating the intrinsic properties of InP nanocrystals from this influence.36

Table 2. Effect of Injection Temperature on the Absorption and Emission Spectra of InP(QDs) When Indium(III) Myristate Is the Precursor

<table>
<thead>
<tr>
<th>Time</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>FWHM (a) (nm)</th>
<th>(\lambda_{\text{em-max}}) (b) (nm)</th>
<th>FWHM (c) (nm)</th>
<th>(\lambda_{\text{em-max}}) (d) (nm)</th>
<th>FWHM (e) (nm)</th>
</tr>
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<tr>
<td>30 s</td>
<td>489 106</td>
<td>na(^{e})</td>
<td>727 204</td>
<td>na(^{e})</td>
<td>699 195</td>
<td>na(^{e})</td>
</tr>
<tr>
<td>1 min</td>
<td>499 99</td>
<td>na(^{e})</td>
<td>729 216</td>
<td>na(^{e})</td>
<td>691 200</td>
<td>na(^{e})</td>
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<tr>
<td>2.5 min</td>
<td>507 98</td>
<td>592 71</td>
<td>735 194</td>
<td>691 200</td>
<td>na(^{e})</td>
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</tr>
<tr>
<td>5 min</td>
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* Full width at half-maximum (FWHM) calculated from absorption spectra.
* Band gap emission. FWHM calculated from the emission spectra.
* Surface state emission. All emission spectra were taken with \(\lambda_{\text{ex}} = 400\) nm, and the emission was recorded from 415 to 785 nm. * Not available.

absorption and emission spectra, it is evident that after 30 s at all temperatures, InP(QDs) have already formed. The lower the reaction temperature, the more blue-shifted the absorption feature, implying that the lower the reaction temperature, the smaller the resulting InP(QDs). Over time, the absorption feature red shifts at the various temperatures. At temperatures greater than 270 °C, the absorption feature becomes broad and featureless, implying a dramatic increase in the size distribution. However, at temperatures below 260 °C, the absorption feature remains sharp throughout the entire 45 min. Each reaction was followed for a total of 2 h and exhibited a sharp absorption feature throughout the entire reaction.

The important thing to note is that, regardless of reaction temperature, a sharp absorption feature is apparent for at least a brief period of time. Typically, when relatively monodispersed crops of nanocrystals are being synthesized, a rapid injection of the group V or group VI precursor is required to generate a rapid crop of reactive nuclei. Then typically, the reaction temperature is decreased to a “growth temperature” until the reaction is stopped. Since with InP(QDs) the reaction temperature, the more blue-shifted the absorption feature, we had a much better control of the final InP(QDs) quality. This study shows that a decrease in the injection temperature was maintained under the exact same conditions and concentrations, and monitored for 2 h. Only the data for the first 15 min are given in Table 3. An example of the absorption spectral monitoring of an entire reaction conducted at 260 °C is shown in Figure 9.

When the reaction temperature is 260 °C, a sharp absorption feature is prominent for up to 45 min. At or slightly after this time, the absorption broadens. When the reaction temperature is 290 °C, this broadening occurs faster, for indium(III) laurate, at or slightly after 15 min. This broadening is a result of “defocusing of size”, resulting in a loss of control over the monodispersity. As the reaction progresses, once all the InP(nuclei) are used up, the individual InP(QDs) begin to react to form larger particles, thereby yielding particles with uncontrolled size. For these reasons, only the spectra of aliquots up to 15 min are presented in Table 3. Evolution of the PL spectra with a change in the carboxylate size and growth temperature, for a given reaction, mirrors the evolution of the absorption spectra. A significant broadening of the sharp PL feature, associated with band edge recombination, is observed when the size distribution can no longer be controlled.

We believe that regardless of the size of the carboxylate chain length, high-quality InP(QDs) can be prepared. The difference in the various reactions is the size of the InP(QDs) that are obtained, which can be correlated to the wavelength of the absorbance feature. The size distribution is not dramatically affected by the size of the carboxylate chain length, as determined by the width of the absorption feature. These reactions in which the injection temperature was maintained throughout the course of the reaction do not produce high-quality InP(QDs). However, with this information, high-quality InP(QDs) that emit throughout the majority of the visible

<table>
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<th>Time (min)</th>
<th>λmax (nm)</th>
<th>FWHMb (nm)</th>
<th>λem–max (nm)</th>
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<td>751</td>
<td>90</td>
<td>197</td>
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</table>

a Full width at half-maximum (fwhm) calculated from absorption spectra.

b Band gap emission.

c FWHM calculated from the emission spectra.

d Surface state emission. All emission spectra were taken with λex = 400 nm, and the emission was recorded from 415 to 785 nm. * Not available.
The spectrum can easily be prepared. For example, if one desired high-quality InP (QDs) that emit at ≈520 nm then by simply looking at Table 3, you would know to use indium(III) stearate as your indium precursor and inject at 260 °C, then add a reaction equivalent of ODE after 30 s, set reaction temperature to 180 °C, and allow the reaction to proceed for a total of 2 h. To obtain high-quality InP (QDs) that emit at 630 nm, use indium(III) laurate as your precursor, inject at 290 °C and add ODE after 15 min, set the growth temperature to 180 °C, and allow the reaction to proceed for a total of 2 h.

We define high-quality InP (QDs) as particles with the properties shown in the first part of this text. They are relatively monodispersed with moderate luminescence and highly crystalline with no impurities. Their luminescence efficiency can be dramatically enhanced by quenching surface state recombination through HF etching or covering the surface with a wider band gap semiconductor material. Thus, using this synthetic method, relatively monodispersed crops of high-quality InP (QDs) can be easily prepared, with a variable absorption band covering a major portion of the visible spectrum.

Conclusions and Future Work

The synthesis of high-quality InP (QDs) has been accomplished without the need of an added coordinating ligand or surfactant. Using this fast and reproducible synthesis, InP (QDs) that emit throughout most of the visible spectrum can be obtained. This is the first example of the synthesis of relatively monodispersed crops of InP (QDs) without the addition of any surfactants or coordinating ligands. After an HF etching process, highly luminescent InP (QDs) are obtained.

We are currently extending this methodology to the synthesis of all II–VI and III–V quantum dots, as well as to the synthesis of core–shell and multiple layered semiconductor nanoassemblies (i.e., core–buffer–shell).

Acknowledgment. We acknowledge and thank Rich Nowak for the collection and help in the interpretation of the XPS data. We also thank Liping Guo for doing the TEM and ED imaging, Dave Bordan for collecting the XRD data, and Peter Bush for collecting the EDAX data. This work is supported by the Directorate of Chemistry and Life Sciences of Air Force Office Research through DURINT Grant AFOSR 1016565-1-21169.

Supporting Information Available: Photoluminescence emission and excitation spectra of InP (QDs) (Figure S1), energy dispersive X-ray spectrum of pyridine-washed InP (QDs) (Figure S2), effect of reaction temperature on the absorption spectra of InP (QDs) (Figure S3), effect of reaction temperature on the emission spectra of InP (QDs) (Figure S4), effect of carboxylate ligand size on the absorption spectra of InP (QDs) prepared at 260 and 290 °C, respectively (Figure S5), and effect of carboxylate ligand size on the emission spectra of InP (QDs) prepared at 260 and 290 °C, respectively (Figure S6) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(39) To help clarify, in response to a reviewer’s question, Battaglia and Peng27 have demonstrated the preparation of InP (QDs) utilizing a new method in ODE. In this work,27 indium(III) acetate and a fatty acid (long chain carboxylic acid) are placed into a reaction vessel and ODE is added. At some point, all of the precursors become soluble and some new species or multiple new species are formed. Then to this mixture of indium carboxylate–acetate species, is added a phosphine or arson precursor to prepare InP (QDs) or InAs (QDs), respectively. In Battaglia and Peng’s short communication, no work or effort was put forth to prove what the reactive indium species was, and we do not feel that it is our place to discuss what intermediates may have been formed under their reaction conditions. The important message in this article is that pure indium(III) carboxylates are prepared separately and characterized before being treated with pure P(TMS)3 to yield high-quality InP (QDs). Our method is the first example in which one pure indium species is weighed out and placed directly into the reaction vessel whereby that pure species is dissolved in unreactive ODE and treated with a phosphine source. To the best of our knowledge, no other reaction conditions have been able to accomplish this in noncoordinating solvents yielding high-quality InP (QDs).