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Formation of High Quality InP and InAs Nanocrystals in a Noncoordinating Solvent

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ABSTRACT

High quality InP nanocrystals without any size sorting were synthesized in a noncoordinating solvent by strictly controlling the reaction parameters. This synthetic method is much faster, less expensive, and “greener” than any current methods for the synthesis of high quality InP nanocrystals. Fatty acids with well-defined chain lengths as the ligands, a noncoordinating solvent, and a thorough degassing process are critical factors for the formation of high quality InP nanocrystals. The growth of nearly monodisperse InAs nanocrystals through a similar scheme was also observed.

Type III–V semiconductors possess superior electronic and optoelectronic properties in comparison to other semiconductors. For this reason, nanostructures made by MBE-related techniques are dominated by III–V semiconductors. In contrast, studies of colloidal III–V semiconductor nanocrystals are much less advanced in comparison to II–VI systems because of their difficult synthetic chemistry.¹ InP nanocrystals are probably the most studied III–V system in terms of their synthesis,^{2–7} but the quality of the as-prepared InP nanocrystals is dramatically lower than that of typical II–VI systems, such as CdSe nanocrystals.⁸ For example, a typical synthesis of InP nanocrystals took 3–7 days and the as-prepared nanocrystals did not show any distinguishable absorption peak,^{5–7} indicating a broad size distribution. This work intended to explore the synthetic chemistry of III–V semiconductor nanocrystals using InP as a model system at elevated temperatures. We observed that the synthesis of InP nanocrystals is significantly more delicate than that of II–VI semiconductor nanocrystals. Typical procedures, ligands, and precursors with similar compositions for the formation of high quality II–VI semiconductor nanocrystals usually did not work for the growth of InP nanocrystals with an acceptable quality. Within the experimental conditions explored, certain fatty acids with well-defined chain lengths, a noncoordinating solvent, a well-controlled indium-to-ligand ratio, and a thorough degassing process are all critical factors for a successful synthesis of InP nanocrystals with an acceptable quality without any size sorting. Those observations may provide some essential keys for the development of “greener” synthetic methods for other III–V semiconduc-

tor nanocrystals. For example, a similar scheme was successfully developed for the growth of nearly monodisperse InAs nanocrystals.

Octadecene (ODE) was used as the noncoordinating solvent⁹ in the synthesis. Fatty acids with different chain lengths, amines, phosphines, phosphine oxides, and phosphonic acids were tested as pure coordinating solvents and/or ligands in ODE. Indium acetate ($\text{In}(\text{Ac})_3$) and tris(trimethylsilyl)phosphine ($\text{P}(\text{TMS})_3$) were used as the precursors unless specified. The best results for both single and multiple injection reactions of InP nanocrystals were achieved by maintaining a 2:1 indium to phosphorus molar ratio. For the growth of InAs nanocrystals, the arsenic precursor was tris(trimethylsilyl)arsine ($\text{As}(\text{TMS})_3$)¹⁰ and the best results are seen by maintaining a 8:1 indium to arsenic molar ratio. The resulting InP and InAs nanocrystals can be dissolved in typical nonpolar solvents. No size sorting was performed on any of the samples used in the measurements.

For a typical synthesis of InP nanocrystals, $\text{In}(\text{Ac})_3$ (0.1 mmol) was mixed with 0.3 mmol of ligands and ODE in a three-neck flask. The mixture, 5 g in total, was heated to 100–120 °C to obtain an optically clear solution and pumped for 2 h using a mechanical vacuum pump. The system was purged with Ar three times, and then further heated to 300 °C under Ar flow. $\text{P}(\text{TMS})_3$ (0.05 mmol) was dissolved in ODE in a glovebox, 2 g in total, and injected into the hot reaction flask. After the injection, the temperature was dropped down to 270 °C for the growth of the InP nanocrystals. For multiple injections, successful secondary injections were performed dropwise at 250 °C by alternating 1 g injections of indium and phosphorus solutions in half the molar concentration of the original. This is done to

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maintain the indium-rich reaction. Aliquots were taken at different reaction times to monitor the reaction. The resulting InP nanocrystals can be dissolved in typical nonpolar solvents. Acetone and methanol were used to precipitate the nanocrystals in order to remove starting materials and side products. No size sorting was performed on any of the samples used in the measurements. XRD and TEM measurements were also performed to characterize the crystallinity, size, and size distribution of the resulting crystals.

Synthesis of typical II–VI semiconductor nanocrystals through most of the “greener” approaches can be performed under Ar flow without degassing the reaction system.^{11–13} For the synthesis of CdS nanocrystals in ODE, the entire process can even be performed in air without sacrificing the quality of the nanocrystals.⁹ In contrast, a thorough degassing step was found to be essential for the synthesis of InP nanocrystals, indicating that InP nanocrystals are extremely sensitive to the atmosphere.

The elements sulfur, selenium, and tellurium dissolved in organophosphine or ODE were broadly used as the precursors for the synthesis of II–VI semiconductor nanocrystals.^{9,13,14} Elemental phosphorus, however, was not active enough to initiate the formation of InP nanocrystals in a variety of coordinating solvents or in ODE. In₂O₃, unlike CdO,^{9,13} was also not found to be feasible for the synthesis of InP nanocrystals because it is insoluble with the desired ligands in ODE (see below).

The formation of monodisperse nanocrystals in solution relies on the principle called “focusing of size distribution”.¹⁰ Based on the current understanding of the focusing of size distribution,^{10,15} a controllable synthesis requires a quick and short nucleation process followed by a relatively slow and long growth process. A quick and short nucleation period should provide the system enough seeds with a relatively narrow size distribution as the starting point. If the growth process that followed was slow enough, there would be enough time to easily tune the resulting nanocrystals. Because the chemical reactivity of the relatively small particles in the solution is greater than that of the relatively large ones for either reaction-controlled or diffusion-controlled growth processes, the relatively small particles should grow faster than the relatively large ones. As a result, the size distribution of the resulting nanocrystals should narrow down as long as no “defocusing of size distribution” occurs.¹⁰ This principle was used as a basic guideline for optimizing synthetic schemes for InP nanocrystals as we did for II–VI systems.⁸

Many types of surfactants/ligands, such as fatty acids, amines, phosphonic acids, phosphines, and phosphine oxides,^{16,17} were found to be good ligands for the synthesis of CdSe, CdS, and CdTe nanocrystals through those “greener” synthetic routes in either coordinating or noncoordinating solvents. Most of those ligands, however, did not work for the growth of high quality InP nanocrystals. For relatively weak ligands, such as amines, phosphine oxides, and some of the fatty acids, a continuous nucleation was found inevitable. With strong ligands, such as phosphonic acids, no reaction was observed under the typical reaction condi-

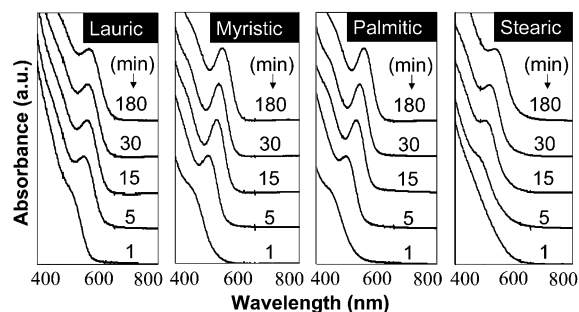


Figure 1. Temporal evolution of the UV–vis spectra of InP nanocrystals grown with fatty acids as the ligands. In/acid ratio = 1:3 for all reactions.

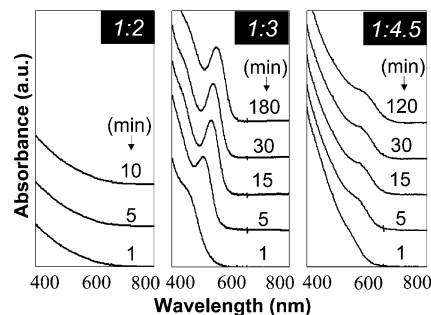


Figure 2. Temporal evolution of the UV–vis spectra of InP nanocrystals grown at 270 °C with different In/MA ratio in ODE.

tions. Coordinating solvents always generated nanocrystals without a distinguishable absorption peak in the UV–vis absorption spectrum, implying a broad size distribution. Among all ligands tested, fatty acids with certain chain lengths were found to be the best ligands using ODE as the noncoordinating solvent. Figure 1 illustrates the temporal evolution of the UV–vis absorption spectra of InP nanocrystals formed in ODE using fatty acids with different chain lengths as the ligands. Evidently, palmitic acid (PA) and myristic acid (MA) are the best fatty acids. Typically, the longer the hydrocarbon chain, the slower the nucleation and growth will be. Likely, the fatty acids with intermediate chain lengths, PA and MA, are the best ligands for the balanced nucleation and growth rate desired for the growth of relatively monodisperse InP nanocrystals.

We reported recently that the concentration of the ligands in a noncoordinating solvent could tune the reactivity of cadmium and zinc precursors to reach the desired balance between nucleation and growth for the formation of high quality II–VI semiconductor nanocrystals.⁹ For InP nanocrystals, the effect of the concentration of the ligands is even more dramatic than the cases of II–VI semiconductor nanocrystals. Figure 2 shows that when the molar ratio of In/MA in the solution was 1:3, the reaction generated InP nanocrystals with a good size distribution indicated by the well-distinguished absorption features. When this molar ratio was varied to either 1:2 or 1:4.5, the reaction was out of control or generated nanocrystals without any distinguishable absorption peak, implying a broad size distribution. This result indicates that the ligand concentration window for the formation of high quality InP nanocrystals, possibly also for other types of III–V nanocrystals, is very narrow.

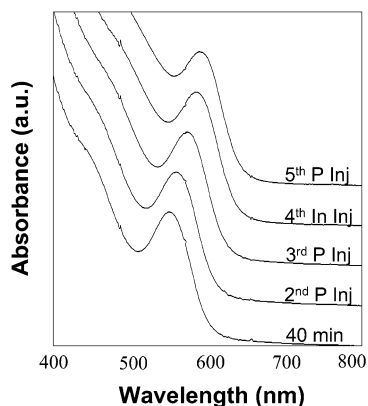


Figure 3. UV-vis spectra of InP nanocrystals grown by multiple injections. A secondary injection was performed after the nanocrystals grew for 5–10 min without changing the absorption spectrum.

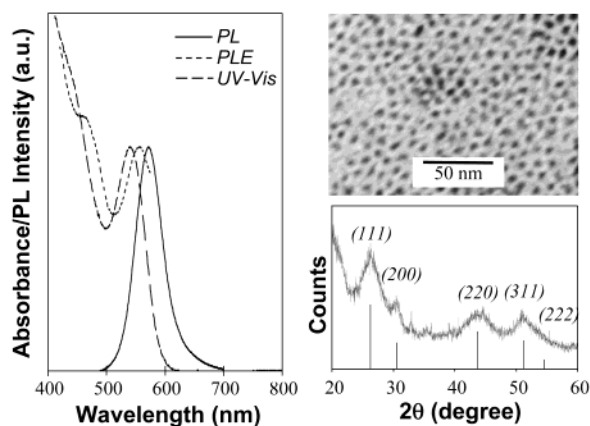


Figure 4. (left) PL, photoluminescence excitation (PLE), and UV-vis spectra of InP nanocrystals. (right-top) TEM image of InP nanocrystals. (right-bottom) XRD pattern of InP nanocrystals.

Secondary injections used commonly for the growth of II–VI nanocrystals¹⁰ after implementing some restrictions were found feasible for varying the size of the resulting InP nanocrystals as demonstrated in Figure 3. The reaction temperature must be reasonably low (at 250 °C or below) for the secondary injections, and the indium precursor and phosphorus precursor must be added separately in an alternating manner. Secondary injections at 270 °C, the growth temperature after the primary injection, or with indium and phosphorus precursors in one solution always resulted in a broad size distribution because of the continuous nucleation caused by the secondary injections.

The photoluminescence (PL) of the InP nanocrystals is solely band-edge emission (Figure 4 left). The PL quantum yield has not reached a high value yet, and the current values are likely about a few percent or lower. Transmission electron microscope (TEM) images of InP nanocrystals revealed that the crystals are generally in a dot-shape mixed with some slightly elongated shapes (Figure 4, top-right). Further shape control of InP nanocrystals is in development. The size of the nanocrystals shown in Figure 4 is $3.1 \text{ nm} \pm 4.7\%$ by measuring 350 nanocrystals. The powder X-ray diffraction (XRD) pattern of the InP nanocrystals matches that of the

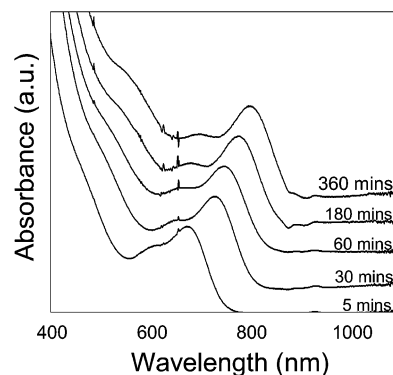


Figure 5. Temporal evolution of the UV-vis spectra of the as-prepared InAs nanocrystals grown in ODE.

zinc blende structure of bulk InP crystals, including the (200) diffraction peak, which is often difficult to resolve^{5–7} (Figure 4, bottom-right).

A similar synthetic scheme also worked for the synthesis of InAs nanocrystals, and the details will be reported later. The preliminary results shown in Figure 5 reveal that the absorption spectra of the as-prepared InAs nanocrystals are very sharp, indicating that the size distribution of the samples is exceptionally narrow in comparison to the ones grown in the traditional coordinating solvents.¹⁰

The size ranges of both InP and InAs nanocrystals achieved at present stage are quite limited. For InP nanocrystals, the first exciton absorption peak in their absorption spectra typically appeared between 500 and 600 nm. The first exciton absorption peak of the InAs nanocrystals grown in the focusing window ranged from 600 to 900 nm. Further development of the synthetic chemistry of III–V semiconductor nanocrystals in noncoordinating solvents is in progress to achieve a better shape control, a higher PL quantum yield, and a larger size range for the as-prepared nanocrystals. The details will be reported later.

In conclusion, a synthetic scheme for high quality InP nanocrystals was successfully developed. This noncoordinating solvent based synthesis generally takes about 3–4 hours per run, which is significantly faster than the existing schemes using coordinating solvents (3–7 days per run).^{5–7} Furthermore, only after tedious size selective precipitation can the size distribution of the InP nanocrystals synthesized through the existing schemes be comparable to that of the as-prepared InP nanocrystals obtained through the new scheme. The new and reproducible scheme is noticeably “greener” and less expensive than the existing schemes since the organophosphine/organophosphine oxide solvent was replaced by ODE in the new scheme. The results further demonstrate that the synthetic strategy in noncoordinating solvents should be generally applicable for the synthesis of other III–V semiconductor nanocrystals. Therefore, the chemistry reported herein should be of critical importance for the advancement of synthetic chemistry for poorly developed III–V nanocrystal systems, which should further promote the fundamental studies¹ and industrial applications¹⁸ of the nanocrystals of those exceptional semiconductors to a desired level.

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