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Rapid Synthesis of High-Quality InP Nanocrystals

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Colloidal III−V semiconductor nanocrystals (NCs) have attracted intense interest within the past 20 years, owing to their less ionic lattice, larger exciton diameters, and reduced toxicity compared to II_B-VI compounds. Nevertheless, the study and application of III−V semiconductor nanocrystals are limited by the difficulty in their synthesis. Because the molecular bonds in III−V semiconductors are more covalent, it is very difficult to obtain a controllable nucleation burst.[1,2] Within the III−V group, the synthesis of InP nanocrystals is the most extensively studied, but until now InP nanocrystals synthesized by current chemical methods did not achieve the same quality as that of most II_B-VI semiconductor nanocrystals.[3−10]

Typical synthesis approaches for III−V semicondutor NCs in a coordinating solvent are adaptations of the method for the II_B-VI group. However, the common coordinating solvents, ligands for II_B-VI system, and the similar precursors do not work well for the synthesis of III−V semicondutor NCs. Both nucleation and crystal growth processes in these approaches needed long reaction times, all together 2−7 days, to yield crystalline particles. In addition, a size-selective process was always necessary.[3−6] Battaglia and Peng developed an efficient method to synthesize InP nanocrystals in a noncoordinating solvent. This method provided a fast, controllable reaction and generated much higher-quality InP nanocrystals.[7] Nevertheless, it is still a challenge to develop a rapid reaction approach in coordinating solvents.

To the best of our knowledge, in noncoordinating solvent routes, the indium precursor was always heated with fatty acids, and the best-quality InP nanocrystals were obtained when the ratio of acid to indium was 3:1.[7,8] High-quality InP nanocrystals were also produced when indium carboxylate was used as precursor without addition of other ligands.[9] Hence, we consider that the carboxylate groups actually acted as an in situ high-selectivity coordination ligand and led to the controllable nucleation and growth processes. On the other hand, in strong coordinating solvents, the unselective coordination of the solvent to indium and phosphorus results in slower and more continuous nucleation. In such a case, it is very difficult to separate the nucleation and crystal growth processes. We supposed that a nucleation process similar to that in noncoordinating solvents could also be obtained in coordinating solvents when the coordinating effect of the solvent is much weaker than that of the introduced strong ligands. We found that high-boiling point esters could be effective weakly coordinating solvents for control of the nucleation process. Further, we tried to accelerate the nucleation burst by proper choice of reagents and reaction conditions, which otherwise possibly limits the use of strong coordinating ligands in producing high-quality InP nanocrystals. Therefore, we devoted our efforts to synthesize InP nanocrystals in weak coordinating solvents. High-quality InP nanocrystals were synthesized via this approach. The as-prepared InP nanocrystals had distinguishable absorption peaks and much narrower size distribution than InP NCs prepared by currently available synthesis methods.

Methyl myristate and dibutyl sebacate were chosen as weak coordinating solvents, because they are nontoxic and relatively inexpensive. Several long-carbon-chain fatty acids and amines were also examined as ligands. Tris(trimethylsilyl)phosphine $(TMS)_3P$ was used as the phosphorus precursor. All chemicals were purchased from Aldrich and have a purity of at least 95%.

For a typical experiment, 1 mL of ester and 0.4−0.45 mmol of ligands were mixed in a three-neck flask and heated to 260 °C under N_2 flow; 0.1 mmol of $(CH_3)_3In$ and 0.05 mmol of $(TMS)_3P$ were dissolved in 0.5 mL of ester to form a clear solution which was rapidly injected into the hot reaction flask. After injection, the solution was cooled and maintained for growth at 200 °C. The products were precipitated and washed with acetone and methanol and redispersed in chloroform. The two esters generated similar quality products.

We started our experiments from repeating the same reaction in the ester as previously published in octadecene (ODE). Indium carboxylate, or different ratios of acid to indium acetate, and $(TMS)_3P$ were used as precursors. The ratio range of indium to phosphorus for these experiments was varied between 1:2 and 4:1. As our prospective result, the produced InP nanocrystals had less distinguishable absorption peaks and broader emission peaks. The full width at half-maximum (fwhm) of the photoluminescence (PL) spectra of the best product was about 85 nm. The lower monodispersity of produced nanocrystals indicates that esters still caused a relatively slower nucleation process than noncoordinating solvents, although they were better than strongly coordinating solvents such as TOPO.

When trimethylindium was used instead of indium carboxylate as the indium precursor, the quality of the InP nanocrystals was dramatically improved with an enhanced PL emission and optimized size distribution. In our experiments, trimethylindium easily dissolved in ester at room temperature and generated a soluble In−ester complex. It is believed that this indium complex had relatively higher activity than indium carboxylate. Therefore, it could react with $(TMS)_3P$ more easily at high temperatures and lead to a higher nucleation rate. We also found the best ligands are fatty acids in our experiments. The temperature influence on our reactions was investigated (Figure 1). The best temperature ranges for injection and subsequent crystal growth processes were found to be 240−280 and 180−210 °C, respectively. Hence, in our further studies, we fixed the injection and growth temperatures to be 260 and 200 °C, respectively, as the standard conditions. The ratio of indium to phosphorus was kept at 2:1 to maintain an indium-rich reaction. When the ratio of fatty acid to indium was 3:1, the fwhm of our produced InP nanoparticles PL spectra was reduced to about 60 nm.

Furthermore, some protic reagents were introduced into the reactions to get a more rapid nucleation burst. It is believed that protic reagents, such as MeOH and RNH_2, hydrolyze $(TMS)_3P$ to accelerate its reaction with indium compounds to produce InP nanoparticles.[4,10] In our study, we tried some amines as protic

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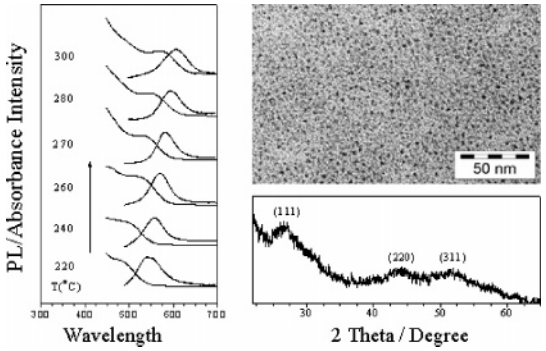


Figure 1. PL and UV−vis absorption spectra (left) of the InP nanocrystal obtained at different injection temperatures after growth for 2 min. TEM image (right top) and XRD pattern (right bottom) of a typical sample. Stearic acid (SA)/indium ratio was 4.2:1 for all the reactions. The mean diameter of the particles in the TEM micrograph is 2.5 nm. Each spectrum was recorded after mixing three batches of samples prepared under identical conditions.

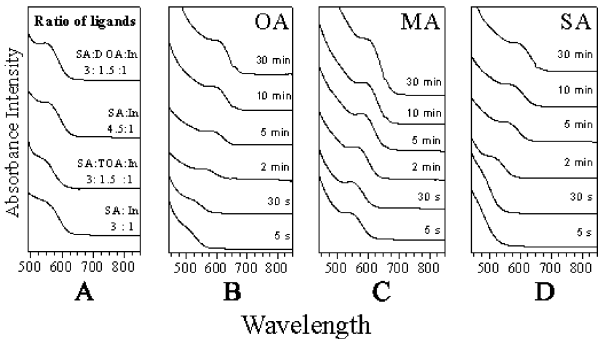


Figure 2. (A) UV−vis spectra of InP nanocrystals obtained with different ratios of ligands, dioctylamine (DOA), trioctylamine (TOA), and stearic acid (SA), after growth for 5 min. (B, C, D) Temporal evolution of the UV−vis spectra of InP nanocrystals grown with different ligands. Ligand/In ratio was 4.2:1 for all reactions.

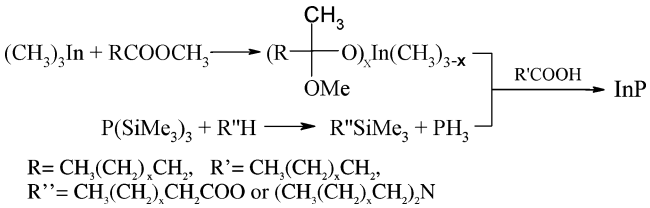
reagents, such as dioctylamine and hexadecylamine. The excessive fatty acid and oleic acid can also serve as protic reagents themselves.

We compared the UV−vis absorption spectra of the nanocrystals obtained in the presence of some different protic and nonprotic reagents. The results are shown in Figure 2 A. When the ratio of stearic acid to indium was 3:1, the absorption spectrum of the as-prepared NCs had an indistinguishable peak. The absorption peak became clear gradually with an increasing content of stearic acid. The best distinguishable absorption peaks were obtained when the ratio was between 4:1 and 4.5:1. Alternatively, when the excessive acid was replaced by the same molar amount of protic reagents, such as dioctylamine (DOA), the as-prepared nanocrystals had a similar quality. However, the replacement of the excessive stearic acid by nonprotic reagents, such as trioctylamine (TOA), resulted in lower-quality nanocrystals.

In the presence of the respective supporting protic reagents, we successfully reduced the fwhm of the PL spectra of resulting InP nanocrystals to about 48 nm. Transmission electron microscope (TEM) images of our samples exhibited that the InP nanocrystals were dot-shaped and very well dispersed. The powder X-ray diffraction (XRD) patterns showed the clear InP nanocrystal peaks of zinc blende structure. Figure 1 depicts one TEM micrograph and XRD pattern of a typical InP sample.

The influence of the hydrocarbon chain length of the fatty acid was studied as well. In noncoordinating solvents, the chain length of the fatty acid had the most distinct effect for the balance of nucleation and growth. The UV−vis spectra of nanocrystals obtained with fatty acids of different chain lengths in these

Scheme 1. Suggested Reaction Scheme



noncoordinating solvents had very obvious differences. In our experiments, we tried three fatty acids with different carbon chain lengths, stearic acid (SA), myristic acid (MA), and oleic acid (OA), as ligands to study the temporal evolution of the UV−vis spectra of the InP nanocrystals. As shown in Figure 2, myristic acid had the best hydrocarbon chain length for the balance of nucleation and crystal growth. However, the three series of spectra did not show as dramatic a difference in the size distribution as observed for synthesis in the ODE system. The results indicate that the influence of the ligand chain length on the reaction has been weakened by some other—more prominent—factors, including the reactive indium precursor and the effect of supporting protic reagents.

Since the hydrolyzation process in our reaction took place at high temperature, resulting in a rapid nucleation burst followed by a slow crystal growth process, it presents a very quick one-pot approach to prepare high-quality InP nanocrystals. It is anticipated, that the protons react with the phosphorus precursor to form in situ highly reactive phosphine which acts as an active phosphorus precursor for generation of high-quality nanocrystals. The reaction pathway through In−ester complex intermediate as shown in Scheme 1 is still under investigation and will be reported in a forthcoming publication.

In summary, a novel and rapid method was developed for the synthesis of high-quality InP nanocrystals via an effective and simple reaction. Fatty acid esters provide a weak coordination condition similar to that by noncoordinating solvents. A highly reactive indium precursor and protic reagents were used to accelerate the nucleation process. The as-prepared nanocrystals had the most narrow size distribution compared to other NCs generated by current methods. Further investigation would extend this method for the synthesis of other III−V and II_B-VI semiconductor nanocrystals.

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