VIP Nanocrystal Synthesis

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Coreduction Colloidal Synthesis of III–V Nanocrystals: The Case of InP**

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Colloidal Group 13–Group 15 semiconductor nanocrystals (III–V NCs) have been the subject of intensive studies during the last two decades because of rich phenomena associated with quantum confinement. However, studies of III–V NCs are restricted owing to synthetic difficulties.[1,2] As a consequence of the attractive applications as luminescence probes for bioimaging and as photovoltaic devices, InP NCs have become the most extensively studied III–V system.[3–14] The synthetic studies of InP NCs are therefore more advanced compared to other III–V systems.

By adaptating Wells' dehalosilylation reaction,[15] some feasible synthetic methods for colloidal InP NCs have been established by several groups.[3–14] These methods usually involve the reaction of an indium salt with tris(trimethylsilyl)phosphine, $P(TMS)_3$, in a high-boiling-point solvent at high temperatures. At first, Mićić et al. chose coordinating solvents (e.g., trioctylphosphine oxide (TOPO) and trioctylphosphine (TOP)) as the reaction medium for the synthesis.[3] To obtain crystalline NCs, growth must be carried out over a long period of time (up to seven days). Even then, the as-synthesized NCs showed a broad size distribution, and a further size-selective post-treatment was required to achieve monodispersity.[5–9,13] Later, Battaglia and Peng further developed this synthesis by replacing the phosphorous-based coordinating solvent with a noncoordinating one, such as octadecene, and using fatty acids as capping ligands.[10] This synthetic variation not only greatly shortened the reaction time to a few hours, but also generated monodisperse InP NCs without any size sorting. Recently, Xu et al. showed that InP NCs of similar quality could also be rapidly produced in some weak coordinating solvents such as fatty-acid esters.[14] However, all of these methods are dependent on the use of expensive $P(TMS)_3$ precursor as the phosphorus source. This results in a high cost, hampering scale-up of the synthesis.

To decrease the cost of the synthesis, a few phosphorous compounds, such as $In(tBu_2P)_3$ and Na_3P, as well as white phosphorus (P_4) have been explored as alternative phosphorus sources.[16–21] However, the replacement of $P(TMS)_3$ by $In(tBu_2P)_3$ or Na_3P leads to much less control over the particle size.[16,17] Moreover, the use of these phosphorus sources brings about some new problems. For example, the synthesis of the organometallic precursor is complex and also high-cost,[16] and the preparation of Na_3P requires a handling of hazardous and pyrophoric sodium metal and P_4.[17] When using the simplest phosphorus source, that is, P_4, the syntheses are usually conducted under hydrothermal or solvothermal conditions;[18–21] the as-synthesized InP NCs are polydisperse and aggregated, giving rise to very low quality. Recently, our group reported that colloidal InP NCs could be prepared using a wet-chemical reduction approach in which P_4 and $LiBH(C_2H_5)_3$ (superhydride) were involved.[22] However, the as-prepared NCs showed a broad size distribution. Therefore, it is still a big challenge to explore an alternative economic phosphorus source for the synthesis of InP NCs of an acceptable quality.

As phosphorus halides, such as PCl_3, can be reduced to elemental phosphorus with extremely high activity, these compounds may be superior phosphorus sources to P_4 for the synthesis of InP NCs. It is anticipated that chemical reaction between freshly reduced indium and phosphorus results in a more rapid nucleation burst, which favors the formation of higher-quality NCs. Herein, we report the first example of using PCl_3 to synthesize high-quality InP NCs through a coreduction colloidal approach. The synthesis was carried out in octadecene in the presence of stearic acid as capping ligand; the reactions involve simultaneous reduction of $In(OAc)_3$ and PCl_3 with superhydride. The hot-injection method, which has been extensively adopted for the colloidal synthesis of monodisperse NCs, is however inapplicable to our system owing to the low boiling point of PCl_3 (76 °C). We thus have to carry out the redox reactions at a low temperature (ca. 40 °C) to retain PCl_3 in the starting solution, and then elevate the temperature for the NC growth.

Figure 1 depicts an X-ray diffraction (XRD) pattern and a transmission electron microscopy (TEM) image of a typical sample grown at 250 °C for 4 h. All detectable diffraction peaks in Figure 1a can be indexed to those of the zinc blende structure InP (ICDD PDF Card No. 73-1983). The broad nature of these peaks indicates the extremely small size of the particles. Figure 1b shows that the InP NCs are dot-shaped and quasi-monodisperse. The average particle size is about (3.5 ± 0.5) nm based on statistical sampling of this image. These results clearly demonstrate that the present synthetic method is effective to generate InP NCs of relatively high quality.

The growth process of InP NCs was investigated by monitoring the UV/Vis absorption spectra of samples grown

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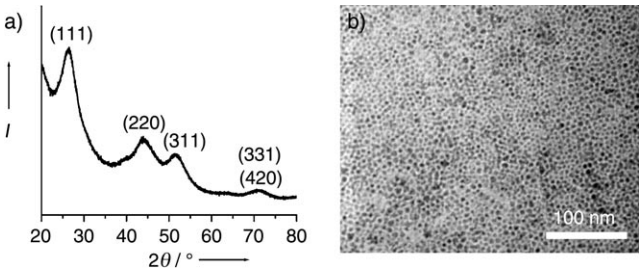

Figure 1. a) XRD pattern and b) TEM image of InP NCs grown at 250 °C for 4 h.

at different times. Figure 2a illustrates the optical absorption spectra of temporally evolved InP NCs grown at 250 °C. It can be seen that an absorption peak is distinguishable for growth

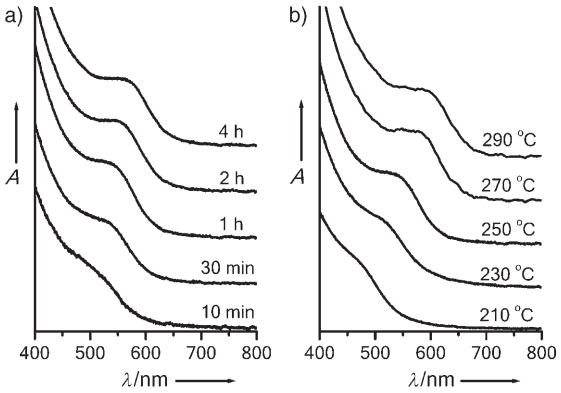

Figure 2. a) Temporal evolution of the UV/Vis absorption spectra of InP NCs grown at 250 °C. b) UV/Vis absorption spectra of InP NCs grown for 1 h at different temperatures.

above 30 min. The emergence of the absorption peak is indicative of a narrow size distribution.[10] As the aging time further increases, the peak is better resolved, and gradually shifts to a longer wavelength. The both features are associated with a narrowing/focusing of the size distribution and a slight increase of particle size over time, respectively. In correspondence with the absorption red shift, the NC colloids have colors varying from orange to deep red.

By controlling the growth temperature, the size of NCs can be further tuned over a wider spectral range, as seen in the UV/Vis spectra (Figure 2b). However, the NCs prepared at a temperatures of <230 °C have a shoulder-like peak or no peak on their absorption spectra, indicating a broad size-distribution, which most likely arises from the poor crystallinity owing to a relatively low growth temperature. On the other hand, the NCs grown at 290 °C also show a broader size distribution than those grown at 250–270 °C. This result suggests the existence of a possible agglomeration at such a high temperature owing to the ultra-fast growth process.

The absorption peaks shown in Figure 2 are not as sharp as those presented by Battaglia et al.[10] in which the InP NCs were prepared using $P(TMS)_3$. This indicates that the present NCs actually have a broader size-distribution than those in the previous work. The lower quality of the NCs may be due to the fact that the reaction between elemental indium and phosphorus involves a slower and more continuous nucleation process. To investigate the possibility of improving the NC quality, we have extensively explored the influences of the solvents and capping ligands. It shows that coordinating solvents (for example, TOPO) always lead to featureless absorption spectra for NCs, implying a very broad size distribution. Noncoordinating solvents, such as hexadecane and dioctyl ether, are generally able to produce higher-quality NCs than coordinating solvents, and the best solvent determined by far is octadecene. On the other hand, fatty acids with shorter hydrocarbon chain lengths, such as myristic and palmitic acids, which yield narrower size distributions than stearic acid does,[10] was found to lack superior ability in control of the size distribution in our case. Thus, additional effort on optimizing the conditions to generate more monodisperse InP NCs is still essential.

The as-prepared NCs exhibited quite weak photoluminescence (PL) compared with the InP NCs prepared with $P(TMS)_3$.[10,11] Their PL spectra contain two emission bands: one at the band edge and a second broader band at longer wavelengths (lower energies), showing the similar feature to those InP NCs prepared using the traditional TOPO method.[5,6,9,13] According to the previous investigations on the both bands,[5,6,9,13,23] the high-energy band is assigned to band-edge recombination and the low-energy band to recombination of surface states. Figure 3a shows a typical PL spectrum from the sample prepared at 250 °C for 4 h. The PL efficiency of this sample is estimated to be ca. 0.25 % on the basis of the band-edge emission. It is generally believed that such low PL efficiency is due to inadequate passivation of the NC surface.[5,9,11,13]

Previous studies have shown that the PL efficiency of InP NCs could be drastically improved by photochemical etching of the NC surface with HF.[5,9,11,13] We thus treated our InP samples with a solution of HF through a modification of the standard method.[5,9,11,13] The comparative results of the PL properties for this typical sample before and after the etching are presented in Figure 3, showing that the HF-etching

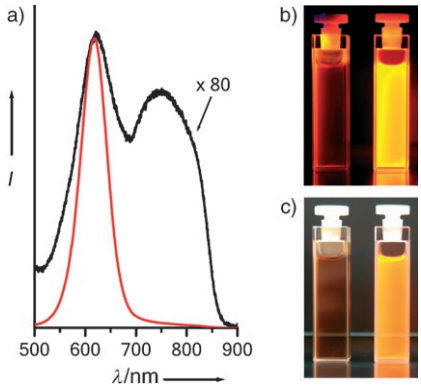

Figure 3. a) Room-temperature PL spectra of InP NCs grown at 250 °C for 4 h before (black line) and after (red line) HF etching. The PL spectra are normalized to an identical absorbance at an excitation wavelength of 366 nm. Photographs of the both colloidal solutions under b) UV illumination (366 nm) and c) UV/white light flash. For both (b) and (c): left, as-prepared NCs; right, after etching.

treatment can remove or passivate the surface states and produce high-efficiency band-edge emission. As shown, the PL intensity is increased by about 80 times after etching, and the emission band becomes much sharper with a full width at half-maximum of ca. 60 nm. The PL efficiency of the etched sample reached about 20%, which is comparable to those of HF-etched InP NCs in previous reports.[5,9,11,13]

In summary, a coreduction colloidal method has been successfully developed for the synthesis of relatively high-quality InP NCs. A post-treatment process with HF could greatly improve the PL efficiency of the NCs. The replacement of expensive or hazardous phosphorus sources, such as $P(TMS)_3$, with a conventional compound, PCl_3, makes the current synthetic approach appreciably greener and more economical. Furthermore, the extension of this synthetic strategy to a general synthetic strategy of other III–V systems shows great promise: We have succeeded in preparation of InAs and InSb NCs using $AsCl_3$ and $SbCl_3$ as the corresponding pnicogen sources.

Experimental Section

All reagents were of analytical grade or better, and were used as received from Aldrich without further purification. Dioctyl ether solution of superhydride ($LiBH(C_2H_5)_3$) was prepared by first mixing the tetrahydrofuran (THF) superhydride solution (1M) with equal volume of dioctyl ether and then evaporating THF under vacuum.

The synthesis of the InP NCs was carried out using standard inert-gas procedures. For a typical synthesis, $In(OAc)_3$ (0.5 mmol) and stearic acid (1.5 mmol) were mixed with octadecene (30 mL) in a three-neck flask. The mixture was heated to 150°C and pumped for 30 min using a mechanical vacuum pump, yielding an optically clear solution. The system was purged with argon and then cooled under argon stream. When the system temperature was dropped to ca. 40°C, 1 mL of octadecene solution containing PCl_3 (0.5 mmol) and dioctyl ether solution of superhydride (1M, 3 mL) were injected in sequence into the flask under vigorous stirring. The resulting mixture was heated to 250°C for NC growth. Aliquots of the reaction mixture were taken at different times to investigate the growth process. Ethanol was used to precipitate the products to remove the byproducts in the reaction mixture. Redispersion of the precipitates in toluene or hexane followed a centrifugation leads to the isolation of colloidal InP NCs.

The etching of the as-prepared InP NCs with HF was performed under ultrasonic conditions in air. Typically, an HF solution (0.2 mL, HF/water/n-butanol 1:2:17 by weight) was added into a toluene solution (10 mL) containing InP NC (ca. 0.1 mmol). The mixture was ultrasonically treated for 30 min. The etched InP NCs were isolated and redispersed by the same procedure for the pristine NCs.

X-ray diffraction (XRD) data of the powder samples (obtained by drying the as-synthesized NCs colloids) were collected using a PANalytical X'Pert system equipped with a Cu Kα radiation source ($\lambda = 0.15406$ nm). TEM images of the samples were obtained from a JEOL-2010 transmission electron microscope. Room-temperature UV/Vis absorption spectra of the samples were recorded using a VARIN Cary 50-Bio UV/Vis spectrophotometer. Room-temperature photoluminescence (PL) spectra of the samples were recorded using a VARIN Cary Eclipse fluorescence spectrophotometer.

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