Synthesis of III-V Nanocrystals by Co-reduction Reactions

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ABSTRACT

This paper describes a co-reduction colloidal method for the synthesis of In-containing III-V nanocrystals (NCs) by using pnictogen halides (such as PCl_3, $AsCl_3$, and $SbCl_3$) as the pnictogen-sources and superhydride ($LiBH(C_2H_5)_3$) as the reducing agent. The syntheses were generally carried out in octadecene in the presence of fatty acids at ~250 ℃. The as-synthesized InP NCs were quasi-monodisperse in particle size and size distribution, whereas the InAs and InSb NCs showed relatively lower quality. The growth process of NCs was studied using InP as a model system.

INTRODUCTION

Colloidal III-V semiconductor nanocrystals (NCs) have attracted intense interest during the last two decades due to their unique effects of quantum confinement. However, chemical synthesis of them is much less advanced compared to the II-VI analogues due to their higher degree of covalent bonding [1-5]. The synthetic methods for III-V NCs are initially developed on the basis of dehalosilylation reactions [6]. These methods usually involve the reaction between a metal salt, such as $GaCl_3$ or $InCl_3$, and tris(trimethylsilyl)pnictogen, $E(TMS)_3$ (E = P, As, or Sb), in a high-boiling-point solvent at a high temperature. Controllable synthesis of III-V NCs was first achieved by the use of coordinating solvents (such as TOPO and TOP) as the reaction media [7-9]. To obtain crystalline NCs, the growth must be carried out over a long period of time (up to seven days) at a temperature ranging from 200-400 ℃. Even then, the as-synthesized NCs showed a broad size distribution, and a further size-selective post-treatment was required to achieve monodispersity. 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 the capping ligands [10]. This synthetic variation not only greatly shortened the reaction time to a few hours but also generated monodisperse InP and InAs NCs without any size sorting. Recently, Xu et al. showed that similar-quality InP NCs could also be rapidly produced in some weak coordinating solvents such as fatty acid esters [11]. However, all of these successful syntheses are dependant on the use of the expensive $E(TMS)_3$ precursors as the pnictogen-sources. This results in a high cost, hampering scale-up of the synthesis.

To lower the cost of the synthesis, some other pnictogen compounds have been explored as the alternative pnictogen-sources. For instance, the decomposition of single-source precursors (organometallic compounds) could directly yield III-V nanocrystals [12,13]; pnictide compounds, $E(Na/K)_3$, were used for the straightforward syntheses of III-V nanocrystals [14,15]. However, the replacement of $E(TMS)_3$ by organometallic compounds or $E(Na/K)_3$ leads to much less control over the particle size. Moreover, the use of the both kinds of pnictogen-sources brings about some new problems. For example, the synthesis of the organometallic precursors is usually complex and also high-cost; the preparation of $E(Na/K)_3$ requires a handling of hazardous and pyrophoric Na/K alloys and elemental pnictogens (especially white phosphorus,

P_4). Furthermore, P_4 or As, as the simplest pnictogen-sources, have also been used for the syntheses of III-V nanocrystals under hydrothermal or solvothermal conditions [16]. However, the as-synthesized NCs are usually polydispersed and aggregated, exposing a very low quality. Recently, our group reported that relatively higher-quality InP NCs could be prepared using a colloidal-chemical approach in which P_4 and superhydride were involved [17]. The as-prepared NCs were discrete and extremely small in size. Nevertheless, their absorption spectra did not show any distinguishable peak, indicating a broad size distribution. Another example of using a simple pnictogen-source was reported by Li et al. Their syntheses of III-V NCs involve the solvothermal reduction of ECl_3 with metallic zinc, indium or gallium in benzene or xylene [18]. However, the as-prepared NCs are low-quality with polydisperse and aggregate features. Therefore, it is still a big challenge both to explore alternative economic pnictogen-sources and to establish a feasible synthetic method for the syntheses of III-V NCs with an acceptable quality.

Recently, we reported a successful synthesis of high-quality InP NCs through a co-reduction colloidal method using PCl_3 as the P-source and superhydride as the reducing agent.[19] In this paper, we further report the general synthesis of InE NCs through the co-reduction colloidal method by using PCl_3, $AsCl_3$, and $SbCl_3$ as the corresponding pnictogen-sources. The syntheses are carried out in octadecene in the presence of stearic acids. Owing to the low boiling points for PCl_3 (b.p., 76 ℃) and $AsCl_3$ (b.p., 130 ℃), we generally conduct the redox reactions at a low temperature in order to retain ECl_3 in the solution and then elevate the temperature for the NC growth.

EXPERIMENT

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 (1 M) with equal volume of dioctyl ether and then evaporating THF under vacuum.

The synthesis was carried out using standard airless procedure. For a typical synthesis, 0.5 mmol of $In(Ac)_3$ and 1.5 mmol of stearic acid were mixed with 30 mL of octadecene in a three-neck flask. The mixture was heated to 150 ℃ and pumped for 30 mins using a mechanical vacuum pump, yielding an optically clear solution. The system was purged with Ar and then cooled under Ar stream. When the system temperature was dropped to ~40 ℃, 1 mL of octadecene solution containing 0.5 mmol ECl_3 (E = P, As, or Sb) and 3 mL of dioctyl ether solution of superhydride (1 M) were injected in sequence into the flask under vigorous stirring. The resulting mixture was then heated for the growth of InE nanocrystals.

For the synthesis of InP NCs, aliquots of the reaction mixture were taken at different times to monitor the growth process. Ethanol was used to precipitate the products in order to remove the byproducts in the reaction solvent. Redispersing the precipitates in toluene or hexane followed a centrifugation leads to the isolation of colloidal InE nanocrystals.

X-ray diffraction (XRD) data of the powder samples (obtained by drying the as-synthesized nanocrystal 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.

DISCUSSION

XRD and TEM Characterizations of InP NCs

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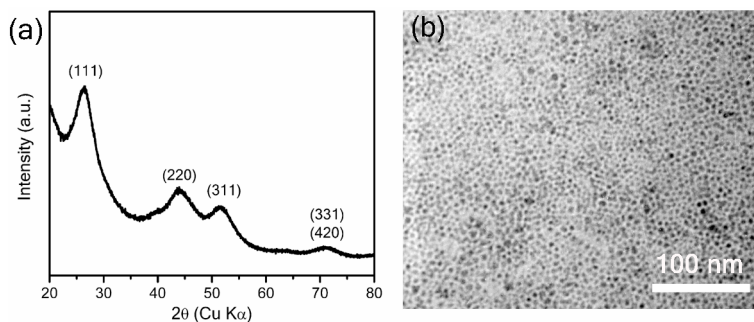

Figure 1. (a) XRD pattern and (b) TEM image of InP NCs grown at 250 °C for 4 h.

Absorption Spectra of InP NCs

The growth process of InP NCs was investigated by monitoring the UV-vis absorption spectra of samples grown at different times. Figure 2a illustrates the optical absorption spectra of temporally evolved InP NCs grown at 250 °C. As displayed, a distinguishable absorption peak can be determined when the growth underwent for up to 30 min. The emergence of absorption peak is indicative of narrow size-distribution.[10] As the aging time further increases, the peak exhibits a higher resolution, and gradually shifts to a longer wavelength. The both features are associated with a narrowing/focusing size distribution and a slight increase of particle size over time, respectively. In correspondence with the red-shift of absorption, the NC colloids present colors varied from orange to deep red.

Through controlling the growth temperature, the size of NCs can be tuned properly in a wider spectral scope, as implied by the UV-vis spectra (Figure 2b). However, the NCs prepared at a temperature of < 230 °C present a should-like peak or no peak on their absorption spectra, indicating a broad size-distribution most likely because of 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 do. This may suggest an existence of a possible agglomeration at such an over-high temperature due to the ultra-fast growth process.
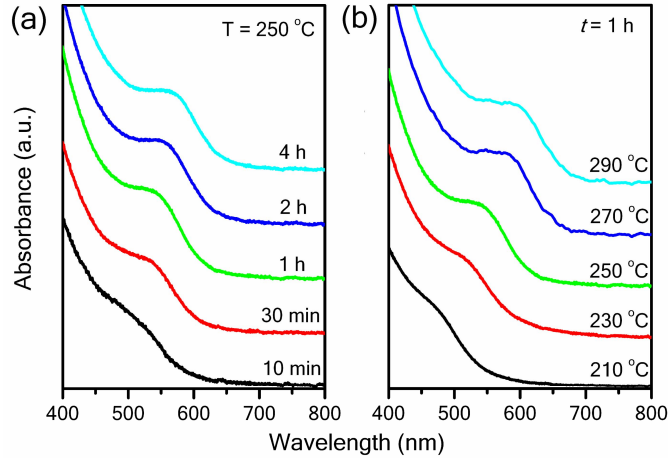
Figure 2. (a) Temporal evolution of the UV-vis absorption spectra of InP NCs grown at 250 ℃. (b) UV-vis absorption spectra of InP NCs grown at different temperatures for 1 h.

PL Property of InP NCs

The as-prepared NCs exhibited quite weak photoluminescence (PL) as 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 a traditional TOPO method.[7c, 8b] According to the previous investigations on the both bands,[7c, 8b, 20] the high-energy band is assigned to band edge recombination and the low-energy band to recombination of surface states. Figure 3 exhibits such a typical PL spectrum from the sample prepared at 250 ℃ for 4 h. The PL efficiency of this sample is estimated to be ~0.25% on the basis of the band-edge-emission. Such low PL efficiency may be a result of inadequate passivation of the NC surface, as reported in the literatures.[21]
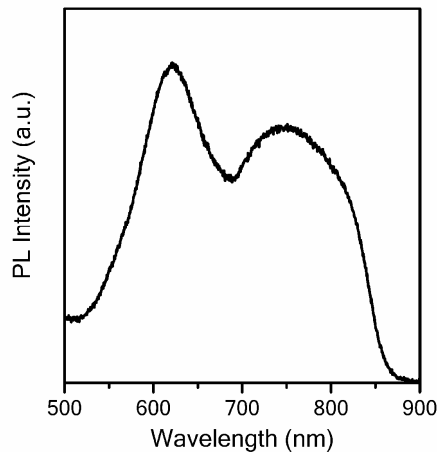
Figure 3. Room-temperature PL spectrum of InP NCs grown at 250 ℃ for 4 h. The PL spectrum is obtained at an excitation wavelength of 366 nm.

Synthesis of InAs and InSb NCs

We have extended such a co-reduction colloidal method for the synthesis of InAs and InSb NCs respectively using AsCl$_3$ and SbCl$_3$ as the corresponding As- and Sb-sources. XRD results (see Figure 4) demonstrate the success on the synthesis of zinc blende InAs and InSb NCs. Nevertheless, the diffraction peaks are relatively narrower compared to those of the pattern of InP NCs, indicative of relatively larger sizes. Moreover, our TEM observations revealed that these NCs had large size distribution and showed an aggregated feature. The relatively lower quality of InAs and InSb NCs may be due to the relatively lower activity of the renascent As and Sb compared to the elemental P.
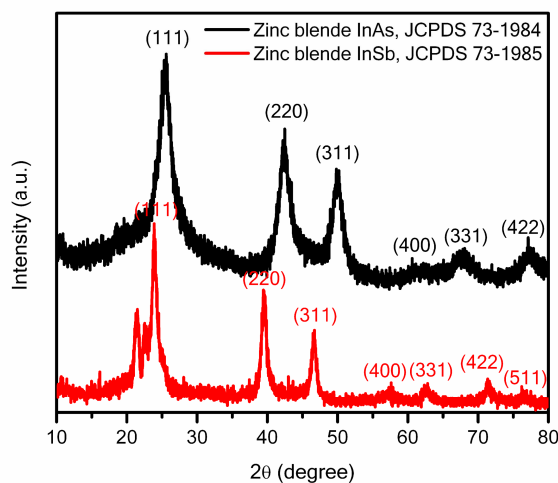
Figure 4. XRD patterns of InAs and InSb NCs grown at 250 ºC for 2 h.

CONCLUSIONS

In summary, a co-reduction colloidal method was successfully developed for the synthesis of In-related III-V NCs. The replacement of expensive or more hazardous pnictogen-sources such as silylated pnictide precursors with conventional compounds, pnictogen tricholride, makes this synthetic strategy noticeably "greener" and more economical, although additional efforts on optimizing the synthetic conditions to produce monodisperse InAs and InSb NCs are still required. Furthermore, it is highly promising to extend this approach to general syntheses of Ga-containing III-V NCs.

ACKNOWLEDGMENTS

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