Facile Preparation of Highly Luminescent InP Nanocrystals by a Solvothermal Route

Chunliang Li, Masanori Ando, and Norio Murase*
Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST),
Ikeda, Osaka 563-8577

(Received April 30, 2008; CL-080447; E-mail: n-murase@aist.go.jp)

Monodisperse InP nanocrystals were prepared by a facile one-pot solvothermal route via the pyrolysis reaction between indium chloride and tris(dimethylamino)phosphine at relatively low temperatures (150–180 °C). The InP nanocrystals after size-selective precipitation had a well-crystallized zinc blende structure, a narrow size distribution, and distinguishable absorption peaks. Application of HF treatment in combination with photoetching increased their emission efficiency to 58% while their emission wavelengths were tunable from green to red.

Emitting semiconductor nanocrystals (NCs) have attracted a great deal of research interest because of their unique optical properties originating from the quantum confinement effect, leading to their application to light-emitting diodes, lasers, and biological labels.[1] The II–VI NCs such as CdS, CdSe, and CdTe are the most studied NCs mainly owing to the relative easiness of the fabrication.[1,2] However, wider applications of these NCs are restricted because of their toxicity. InP NCs have a wide wavelength tuning range with stronger covalent bonds originating from III–V nature and less toxicity than II–VI NCs. Therefore, they are studied most extensively among all other colloidal III–V NCs.

InP NCs has been obtained through the dehalosilylation reaction between indium chloride (InCl$_3$) and tris(trimethylsilyl)-phosphine in the presence of a coordinating solvent such as trioctylphosphine oxide, trioctylphosphine, or dodecylamine (DDA).[3–7] They were initially prepared using one-pot synthesis at temperatures over 250 °C.[3] A hot injection technique was then developed that enabled their nucleation stage to be separated from their growth stage.[4–7] High-quality InP NCs have been obtained using fatty acid as the ligand in noncoordinating solvent.[5] Since InP has covalent bond nature, these synthesis methods are complex, requiring a high reaction temperature ($>$200 °C), several days for reaction, and an oxygen-free atmosphere.

Numerous investigations have thus been made on various preparation routes in order to obtain high-quality InP NCs without using complex reactions or toxic flammable precursors.[8,9] Matsumoto et al. made InP NCs using a safe and easily available phosphorus source (tris(dimethylamino)phosphine, P(N(CH$_3$)$_2$)$_3$) while using the traditional TOPO method described above at 300 °C.[8] The resulting NCs had a diameter of 6.4 nm with a size distribution of $\approx$50% and showed featureless absorption and broad photoluminescence (PL) spectra. Solvothermal (or hydrothermal when the solvent is water) synthesis is another method for preparation synthesis of semiconductor NCs, providing a short reaction time at low temperature. Qian et al. obtained InP NCs using both solvothermal and hydrothermal methods.[9] However, these NCs were mainly in the form of secondary particles, and their PL efficiencies were quite low. Moreover, the phosphorus source (Na$_3$P or P) is highly toxic and flammable.

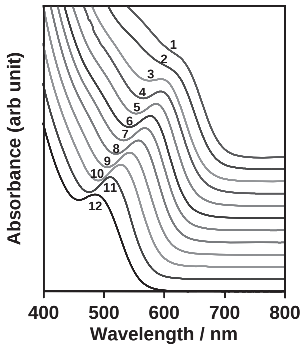

Figure 1. Absorption spectra of solvothermally synthesized InP NCs after size-selective precipitation (up to 12 monodisperse fractions).

We have successfully prepared monodisperse InP NCs using a one-pot solvothermal method and a safe phosphorus source. The method is simple and safe, and all the operations are carried out in air except for the weight measurements of the chemicals. The PL of the size-selected NCs is drastically increased by hydrogen fluoride (HF) treatment in combination with photoetching.

In a typical synthesis procedure, InCl$_3$ (1.81 mmol), P(N(CH$_3$)$_2$)$_3$ (2.75 mmol), and DDA (27 mmol) are well mixed with 5 mL of toluene and placed in a 50-mL Teflon-lined autoclave in a glovebox under an argon atmosphere. The autoclave is sealed and taken out of the glovebox. The autoclave is then heated to 70 °C for 1 h to dissolve the InCl$_3$ and DDA into the toluene solvent. It is subsequently kept at 180 °C for 24 h and then cooled to room temperature. DDA is known to act as a good stabilizing agent for preparation of semiconductor NCs.[5] This reduces the temperature of NC formation.[10] P(N(CH$_3$)$_2$)$_3$ is a safe and readily available phosphorus source.[8] This material decomposes at low temperatures to provide phosphor. Solvothermal synthesis further reduces the required reaction temperature. After the by-products are precipitated and discarded, the crude solution is subjected to size-selective precipitation using toluene and methanol as the solvent and nonsolvent, respectively. The photoetching of the NCs with HF is done by changing irradiation wavelength and power from those previously reported.[11] During etching, the NCs are irradiated with ultraviolet (UV) light (365 nm, 2 W/cm^2). The PL efficiencies of the NCs are estimated using the recently reported method.[12]

The as-prepared InP NCs had a broad size distribution because the nucleation and growth occurred simultaneously during the solvothermal synthesis. After the precipitation, the size-selected NCs had a size distribution as narrow as 10% (as explained below) and showed distinguishable excitonic peaks in the absorption spectra as shown in Figure 1. As the size of

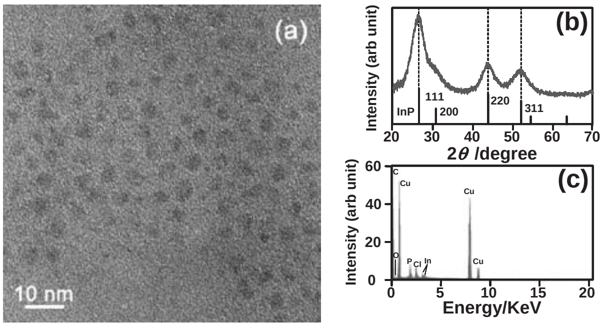

Figure 2. High-resolution TEM image (a), XRD patterns (b), and EDX analysis results (c) for InP NCs after size-selective precipitation. Bars at bottom in (b) represent peak positions of bulk InP.

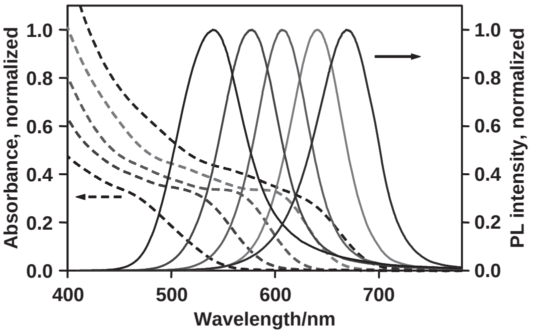

Figure 3. Absorption and PL spectra of InP NCs after HF treatment combined with UV-light photoetching.

the NCs increased, the absorption spectrum shifted to red, and the excitonic peaks changed to shoulders. The particle sizes of the NCs roughly ranged from 2 to 4 nm, as determined from the absorption peak and reported values.[3,11] That is, InP NCs of different sizes were obtained simultaneously. Moreover, InP NCs with small particles sizes were obtained when the reaction temperature was reduced to 150 °C.

Figure 2a shows a transmission electron microscopy (TEM) image of a typical fraction of InP NCs after size-selection. The NCs were round and well dispersed. The average particle size obtained from the images was 3.1 ± 0.3 nm. Powder X-ray diffraction (XRD) patterns of the InP NCs are shown in Figure 2b. The detected peaks corresponded to InP of a zinc blende structure. The particle size was estimated to be 3.4 nm from application of the Debye–Scherrer equation. This closely agrees with the size obtained from the TEM images. The existence of In and P elements in the NCs was also confirmed using energy-dispersive X-ray (EDX) analysis (Figure 2c). Elemental analysis for size-selected InP NCs (Figure 2a; 3.1 nm) was carried out using electron probe microanalysis. The results show that they were In rich with an In/P molar ratio of 1.7. Given the particle size, roughly half of the atoms were on the surface of the particle. This indicates that the surfaces of the prepared InP NCs were covered mainly with In atoms.

Because the as-prepared InP NCs usually showed poor PL efficiencies (<0.1%), they were treated with HF in combination with photoetching. The treatment was completed within a few minutes by using high-power UV light. Figure 3 shows the absorption and PL spectra of HF-etched InP NCs of various sizes. The first excitonic peaks were a bit smoother and featureless after HF treatment in comparison with those after size-selective precipitation (Figure 1). The PL efficiencies of the NCs were drastically improved after the HF treatment (see Table 1 for details). This phenomenon has been reported for differently prepared InP NCs.[11] The red sample had PL efficiencies of nearly 60%, which is the highest value ever reported for InP NCs. The investigation to make the NCs luminescent in water without using HF is currently in progress.

Table 1. PL properties of InP NCs after photochemical HF treatment for samples shown in Figure 1

Sample	ϕ^a/nm	λ_{PL}/nm	η/%	FWHM^b/nm
1	4.0	666	30	68.6
4	3.5	641	58	60.0
7	3.1	607	47	59.4
9	2.7	578	40	64.4
11	2.3	540	27	73.2

[a]Particle size of NCs just before HF treatment. [b]Full width at half maximum.

In conclusion, we have developed a one-pot solvothermal method for preparing high-quality InP NCs using the pyrolysis reaction between $InCl_3$ and $P(N(CH_3)_2)_3$ in a mixture of DDA and toluene at low temperature. The advantage of the method is its simplicity, safety, and low cost. After size-selection, InP NCs have a well-crystallized zinc blende structure, a narrow size distribution, and distinguishable absorption peaks. When the photochemical HF treatment was developed, their PL efficiencies became as high as 58% while their PL peaks were tunable from green to red. This method can be extended to the preparation of other III–V and II–VI semiconductor NCs.

This study was supported in part by the Creation and Support Program for Start-ups from Universities, sponsored by the Japan Science and Technology Agency (JST).

References

1 V. L. Colvin, M. C. Schlamp, A. P. Alivisatos, *Nature* **1994**, *370*, 354; V. I. Klimov, A. A. Mikhailovsky, S. Xu, A. Malko, J. A. Hollingsworth, C. A. Leatherdale, H. J. Eisler, M. G. Bawendi, *Science* **2000**, *290*, 314; W. C. W. Chan, S. M. Nie, *Science* **1998**, *281*, 2016.

2 C. B. Murray, D. J. Norris, M. G. Bawendi, *J. Am. Chem. Soc.* **1993**, *115*, 8706; J. E. B. Katari, V. Colvin, A. P. Alivisatos, *J. Phys. Chem.* **1994**, *98*, 4109; N. Gaponik, D. V. Talapin, A. L. Rogach, K. Hoppe, E. V. Shevchenko, A. Kornowski, A. Eychmüller, H. Weller, *J. Phys. Chem. B* **2002**, *106*, 7177; C. Li, N. Murase, *Chem. Lett.* **2005**, *34*, 92.

3 O. I. Mićić, C. J. Curtis, K. M. Jones, J. R. Sprague, A. J. Nozik, *J. Phys. Chem.* **1994**, *98*, 4966; O. I. Mićić, K. M. Jones, A. Cahill, A. J. Nozik, *J. Phys. Chem. B* **1998**, *102*, 9791; O. I. Mićić, S. P. Ahrenkiel, A. J. Nozik, *Appl. Phys. Lett.* **2001**, *78*, 4022.

4 A. A. Guzelian, J. E. B. Katari, A. V. Kadavanich, U. Banin, K. Hamad, E. Juban, A. P. Alivisatos, R. H. Wolters, C. C. Arnold, J. R. Heath, *J. Phys. Chem.* **1996**, *100*, 7212.

5 D. V. Talapin, A. L. Rogach, I. Mekis, S. Haubold, A. Kornowski, M. Haase, H. Weller, *Colloid Surf., A* **2002**, *202*, 145.

6 L. Langof, L. Fradkin, E. Ehrenfreund, E. Lifshitz, O. I. Mićić, A. J. Nozik, *Chem. Phys.* **2004**, *297*, 93.

7 D. Battaglia, X. Peng, *Nano Lett.* **2002**, *2*, 1027; R. Xie, D. Battaglia, X. Peng, *J. Am. Chem. Soc.* **2007**, *129*, 15432.

8 T. Matsumoto, S. Maenosono, Y. Yamaguchi, *Chem. Lett.* **2004**, *33*, 1492.

9 Y. Qian, *Adv. Mater.* **1999**, *11*, 1101; S. Wei, J. Lu, W. Yu, Y. Qian, *J. Appl. Phys.* **2004**, *95*, 3683.

10 N. Pradhan, D. Reifsnyder, R. Xie, J. Aldana, X. Peng, *J. Am. Chem. Soc.* **2007**, *129*, 9500.

11 D. V. Talapin, N. Gaponik, H. Borchert, A. L. Rogach, M. Haase, H. Weller, *J. Phys. Chem. B* **2002**, *106*, 12659.

12 N. Murase, C. L. Li, *J. Lumin.* **2008**, in press. doi: 10.1016/j.jlumin.2008.05.016.

Published on the web (Advance View) July 12, 2008; doi:10.1246/cl.2008.856