Organometallic Synthesis of InP Quantum Dots Using Tris(dimethylamino)phosphine as a Phosphorus Source

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InP colloidal quantum dots (QDs) were synthesized via an alternative synthetic route. Pyrolysis of indium trichloride and tris(dimethylamino)phosphine [$P(NMe_2)_3$] in a mixture of trioctylphosphine and trioctylphosphine oxide gives InP QDs with an average diameter of a few nanometers. The InP QDs were characterized by TEM, XRD, X-ray fluorescence analysis, UV–vis, and fluorescence spectrophotometry. The synthetic method using $P(NMe_2)_3$ as a phosphorus source is safer and more facile than other existing methods to synthesize InP QDs.

Colloidal quantum dots (QDs) are promising materials because optical and electric properties can be tuned substantially by varying their size.[1] Thus, synthetic methods and optical and electric properties of QDs have been actively investigated for decades.[2] Such investigations, however, have placed a disproportionate emphasis on II–VI QDs, mainly due to the ease of their synthesis. InP has superior electric conduction properties in III–V semiconductors, and is a promising material for microwave devices,[3] optoelectronics,[4] etc. Several synthetic routes for InP QDs, e.g. pyrolysis of single-molecular precursors[5] and direct reaction using sodium phosphide,[6] have been proposed. The most established method is probably the pyrolysis of indium trichloride ($InCl_3$) and tris(trimethylsilyl)phosphine [$P(SiMe_3)_3$] in a mixture of trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO).[7,8] However, $P(SiMe_3)_3$ has the drawbacks of low stability, high flammability, and limited availability. In view of this situation, an alternative synthetic method for InP QDs is proposed, using tris(dimethylamino)phosphine [$P(NMe_2)_3$] as the phosphorus source, as this is safer and more readily available than $P(SiMe_3)_3$.[9]

$InCl_3$ (purity 99.999%), TOP (90%), and TOPO (99%) were purchased from Aldrich Chemical Company, Inc. $P(NMe_2)_3$ (98%) was purchased from Wako Pure Chemical Industries. The synthesis was carried out by following the method proposed by Nozik and co-workers,[8] with some modifications. $InCl_3$ (0.8 g) and $P(NMe_2)_3$ (0.5 g) were dissolved in 5 g of a TOPO/TOP mixture under standard inert conditions (stock solution). Two stock solutions with different TOPO/TOP volume ratios were prepared: (a) TOPO:TOP = 0.15:1 and (b) TOPO:TOP = 1:1. In addition, 5 g of a TOPO/TOP mixture was put into a three-neck flask and heated up to 100 °C. The TOPO/TOP volume ratios were the same as those of the stock solutions. The flask was then evacuated for 20 min to remove oxygen and volatile components from the TOPO/TOP matrix. After the evacuation, the flask was purged three times by high-purity Ar. Subsequently, the temperature was raised to 345 °C under an Ar atmosphere. At 345 °C, the stock solution was rapidly injected into the flask. Immediately after the injection, the reactant turned orange and then brown. Shortly thereafter, the temperature was changed to 300 °C and the mixture was kept at this temperature for 1 h. All reagents were handled under a strictly oxygen- and water-free environment. After 1 h of reaction, 1-butanol and methanol (anhydrous) were added into the flask at room temperature. By centrifuging this mixture, a blackish brown powder was separated from the TOPO/TOP matrix. This product was stored under vacuum to prevent oxidation of the QDs.

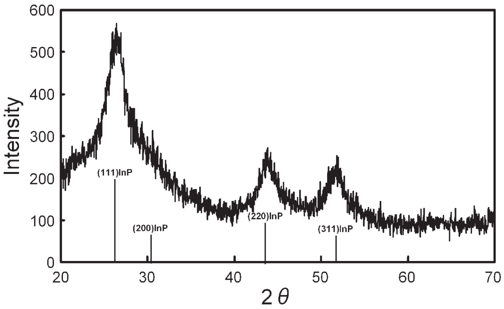

Figure 1. XRD pattern of InP QDs synthesized using stock solution (a).

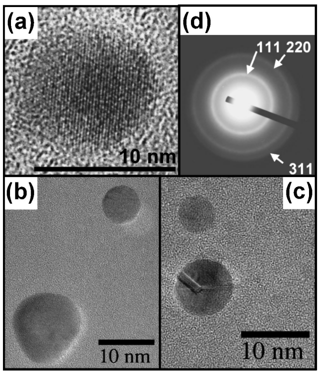

Figure 2. High-resolution TEM micrographs of (a) a single InP QD and (b-c) other InP QDs. The size distribution of the QDs is about 50%. Part d shows the SAED pattern of QDs.

Structural analysis of the synthesized QDs was performed using transmission electron microscopy, selected area electron diffraction (SAED), and X-ray diffractometry (XRD) using Cu Kα radiation. Composition analysis of QDs was carried out using a JEOL JSX-3220 energy-dispersive X-ray fluorescence spectrometer (XRF). Absorption and photoluminescence (PL) spectra of QDs were obtained by using a Hitachi U-4100 UV–vis spectrophotometer and a Jasco FP-6500 fluorescence spectrophotometer.

Figure 1 shows the XRD pattern of QDs, which were deposited on a glass substrate by drying a hexane suspension of QDs synthesized using stock solution (a). As seen in Figure 1, three distinct peaks are observed coinciding with, starting from the left, (111), (220), and (311) reflections of a bulk InP crystal. The halo-like background observed at a lower angle is due to the glass substrate. The 2θ values of each diffraction peak are, starting from the left, 26.2, 46.3, and 51.7 degrees. By applying the Scherrer formula to the (111) peak, the average diameter of the InP QDs is estimated to be 3.3 nm. The TEM micrograph of the InP QDs synthesized using stock solution (a) is shown in Figure 2. Small particles 6.4 nm in average diameter are observed in the TEM micrograph, although the size distribution is found to be broad (size distribution of about 50%). In the case of InP QDs, however, the size distribution of as-synthesized QDs is usually broad (ca. >30%).[10] Thus, the size-selective precipitation is normally carried out before use. After size-selective precipitation, the samples have a size distribution of about 10%. The development of a synthetic route of monodisperse InP QDs should be considered separate issues. The difference in average sizes of InP QDs estimated from the (111) peak of XRD pattern and the TEM image is presumably due to the poor crystallinity of QDs. Part d shows the SAED pattern of the QDs, indicating that the QDs are InP nanocrystallites. Semiquantitative composition analysis of the InP QDs was also carried out by XRF for the QDs synthesized using stock solution (a). The element ratio of the QDs was found to be In:P = 1.25:1. This result is considered reasonable because the molar ratio of $InCl_3$ to $P(NMe_2)_3$ in the stock solution was 1.18, although it appeared to be slightly In rich. Note that the InP QDs were not obtained when $P(NMe_2)_3$ was absent in the stock solution. Hence, we conclude that $P(NMe_2)_3$ is the only phosphorus source.

The absorption and PL spectra of InP QDs dispersed in hexane are shown in Figure 3. An excitation wavelength of 365 nm was used in the PL measurements. Gray and black lines correspond to the absorption and PL spectra, respectively. The spectra of QDs synthesized using stock solutions (a) and (b) are shown in Figures 3a and 3b, respectively. The featureless absorption and broad emission spectra would be due to the size distribution of QDs (6.4 ± 3.2 nm), because the band-gap energy ranges from 1.5 to 2.2 eV.[11] The PL spectrum shifted toward lower wavelengths as the TOPO concentration increased, as shown in Figure 3. It is well known that the InP QDs usually grow large in the absence of the TOPO stabilizer.[7] This indicates that TOPO molecules suppress growth of InP QDs, presumably due to the higher coordinating strength of TOPO molecules than TOP molecules onto the surface of QDs. This result implies that the size of InP QDs can be tuned by varying the TOPO/TOP volume ratio. Note that the sharp peak observed at 412 nm in the PL spectrum of QDs synthesized using stock solution (b) (Figure 3b) is due to Raman scattering of TOPO molecules. It is shifted by $\approx 3000\,\mathrm{cm}^{-1}$ from the excitation wavelength due to excitation of C–H vibrations. The weak Raman peak is always present, and becomes prominent in the case of weakly luminescent samples. The broad shoulder observed at the longer wavelength in the PL spectra is possibly due to radiative recombination via trap sites arising from phosphorus vacancies.[8] This supposition is in accord with the results of the XRF composition analysis.

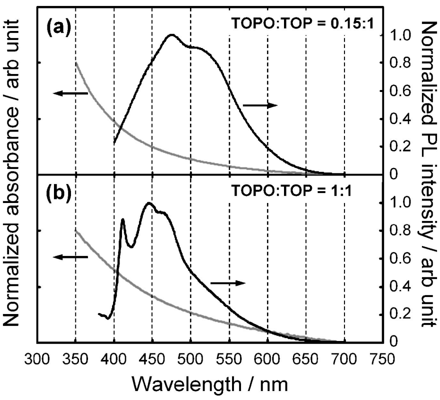

Figure 3. Absorption (gray lines) and PL (black lines) spectra of InP QDs synthesized using stock solutions with different TOPO/TOP volume ratios: (a) TOPO:TOP = 0.15:1 and (b) TOPO:TOP = 1:1.

In conclusion, InP colloidal QDs were synthesized via an alternative synthetic route using $InCl_3$ and $P(NMe_2)_3$ as precursors. The synthesis is based on pyrolysis of the precursors in a mixture of TOP and TOPO. Consequently, TOPO/TOP-capped InP QDs of average diameter 6.4 nm were successfully obtained. Regulation of the QD size would be possible, by varying the TOPO/TOP volume ratio. This synthetic method using $P(NMe_2)_3$ as the phosphorus source is safer and utilizes more readily available material than other existing methods of synthesizing InP QDs. A systematic investigation should be performed to obtain highly monodisperse, high-quality InP QDs, and is currently in progress.

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9 $P(SiMe_3)_3$: U.S. DOT Hazard Class 4.2, Packing Group I (Not permitted for air transport), EU Risk Phrases 17; $P(NMe_2)_3$: DOT Class 3, Packing Group III, EU Risk Phrases 10.
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