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Synthesis of InP quantum dots in dodecylamine from phosphine and indium(III) chloride

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A new synthesis of spherical InP quantum dots in dodecylamine using phosphine as a source of phosphorus was developed.

Nanostructured materials are a rapidly growing field of science where chemists, material scientists and biochemists contribute very much. Quantum dots (QDs) are very promising for constructing photodetectors, solar cells, electroluminescent devices, optical amplifier devices for data transmission in telecommunication and in biotechnology for creating fluorescent biotags.[1] The study of $A^{III}B^{V}$ QDs (namely, InP QDs) is very important because such a material does not contain toxic elements as compared to widely studied CdSe QDs.

Initial attempts to prepare $A^{III}B^{V}$ materials were focused on reaction of separate sources in high-boiling solvents[2] or an electrospray method[3] but the result was disappointing. Micic *et al.*[4] have developed a method of synthesis of tri-*n*-octylphosphine oxide (TOPO) capped InP QDs by thermal decomposition of precursor complex that was later modified.[5,6] Battaglia and Peng[7] have modified the synthetic route by using octadecene as a noncoordinating solvent and fatty acids as nanocrystallic surface stabilizers. Recently,[8] it was shown that quality InP QDs can be rapidly produced in some weak coordinating solvents such as fatty acid esters. To decrease the cost of synthesis, other phosphorus compounds such as $In(Bu^{t}_{2}P)_3$ and Na_3P were proposed,[9,10] but the use of these phosphorus sources brings new problems associated with complexity and safety issues of the experiment. When using white phosphorus, the syntheses of InP QDs are usually conducted under hydrothermal conditions in the presence of strong reducer, $NaBH_4$ for example, and the resulting nanocrystals turn out to be polydisperse and aggregated.[11,12] It is possible to apply phosphorus halides such as PCl_3 and reduce them by $LiBHEt_3$ directly in the reaction mixture.[13]

Thus, the synthesis of InP QDs is rather difficult and prolonged process, which needs high cost precursors. So, the search for and development of the alternate simple and relatively cheap synthetic route to high quality InP QDs is an actual goal for scientists.

A way to simplify the synthesis of InP QDs in organic solvents is to use gaseous phosphine PH_3 as a source of phosphorus. Note that, if one is carrying out the reduction reaction of white phosphorus under hydrothermal conditions, the PH_3 is formed *in situ*, but the resulting InP nanoparticles would be very polydisperse because of the prolonged thermal processing, during which the new particles are formed and that is the integral feature of the synthetic method.

Here, a novel synthetic route to InP QDs using PH_3 in coordinating solvent dodecylamine (DDA) is presented. Anhydrous $InCl_3$, synthesized from elements,[14] was used as a source of indium. $InCl_3$ was dissolved in DDA in pure Ar atmosphere at 200 °C. Phosphine was synthesized by reaction (1), mixed with Ar and passed through the $InCl_3$ solution for 5 min at 200 °C, which led to its orange coloration evolved to nearly black in only a minute. The synthesis of InP QDs can be written as reaction (2). The mixture was maintained at the same temperature for 15 min to decontaminate the solution from the excess PH_3, rapidly cooled and after that acetone was added to precipitate the nanocrystals. The resulting black precipitate was separated from the reaction mixture by a centrifuge. XRD showed that the precipitate was InP, average diameter of crystals according to the Debay–Scherrer equation was about 10 nm. InP precipitate could not form sols in any tried organic solvents; so, it was not studied further. The red-brown colloidal solution after the centrifuge had a green luminescence at UV excitation.

$$Zn_3P_2 + 3H_2SO_4 = 2PH_3\uparrow + 3ZnSO_4 \quad (1)$$

$$InCl_3 + PH_3 \xrightarrow[C_{12}H_{25}NH_2]{200\ ^\circ C} InP\ (QDs, capped\ by\ C_{12}H_{25}NH_2) \quad (2)$$

The red-brown colloidal solution containing InP QDs was to be separated from excess DDA that was preventing further study of the samples. The first separation technique is described below. The initial QD solution containing acetone was added (1:1) to a dilute solution of H_2SO_4 to yield a homogeneous mixture that kept luminescent properties. The acid was neutralized by the alkali solution. The precipitation of DDA started at pH 11–12; then, the solution became layered. The upper oily dark-brown layer was separated and dissolved in chloroform. After that the extraction of DDA by a dilute solution of H_2SO_4 was performed three times. Note that the processing of the QD solution by the acid did not destroy the InP nanocrystals and did not affect the luminescence because of the stabilizer on their surface. The resulting 'clear' QD solution was dropped and dried up forming a film on a Si (100) substrate. XRD showed that the film consists of DDA and a small quantity of nanocrystalline InP, so the clearing process was not fully successful. The resulting QD solution will further be designated as sample A.

The other method of DDA separation consists in the vacuum evaporation of acetone with the subsequent thermal vacuum evaporation of DDA in an oil bath at 200 °C for 3 h. The obtained dry brown-black substance easily dissolved (formed sols) in $CHCl_3$ and slightly worse in hexane (sample B). Obtained solutions had a green luminescence at UV excitation.

Absorption measurements were carried out on a Varian Cary 50 spectrophotometer. Absorption spectrum (Figure 1) of sample A shows a well resolved excitonic peak at ~497 nm (2.49 eV), which corresponds to a mean particle diameter of about 2.2 nm.[6] An ill-defined excitonic peak in the absorption spectrum of sample B at 500 nm could be explained by growth of the par-

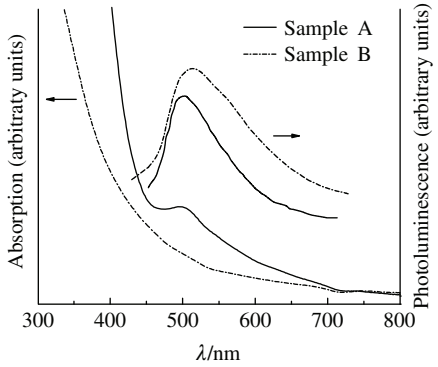

Figure 1 Absorption and photoluminescence spectra of InP QDs.

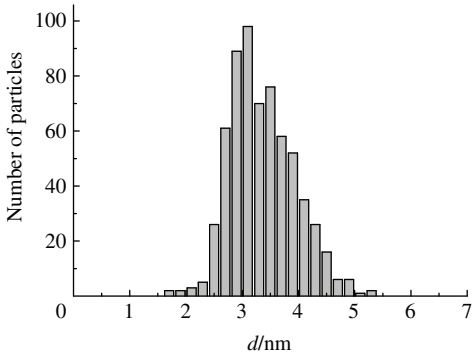

Figure 3 Size distribution of particles in sample B.

ticles and broadening of their size distribution. Looking ahead – the particle size varies from ~2.5 to ~4 nm, which corresponds to wide absorption spectral range about 135 nm,[6] leading to very broad and low-intense absorption peak. Peak in the photoluminescence (PL) spectrum of sample A (excitation at 405 nm) is relatively broad (Figure 1), its maximum position is 502 nm – it is shifted to red spectral region in comparison with the excitonic peak (Stocks shift). The maximum position in the PL spectrum of sample B is 513 nm, but we can hardly define the maximum of absorption peak.

Nanocrystals sizes and morphology from sample B were studied by transmission electron microscopy (TEM) on a LEO912 AB OMEGA microscope (Figure 2). The particles are nearly spherical, the spacings between particles are about 3–5 nm possibly due to presence of DDA on the surface of QDs that cannot be registered by TEM. These spacings are more than two times longer than the length of DDA molecules. The particle diameter distribution (Figure 3) was obtained by statistical processing of TEM image from Figure 2. The mean particle diameter is 3.2 nm, HWHM (half width at half maximum) ~20%. Consequently, the suggestion that thermal evaporation of DDA leads to growth of InP nanoparticles was correct.

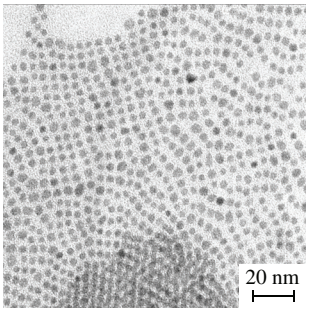

Figure 2 TEM image of sample B.

In conclusion, we have developed a novel synthetic route to InP QDs from $InCl_3$ and PH_3 in dodecylamine as a solvent and particle stabilizer. The QDs are characterized by green luminescence (~500 nm) at excitation (~405 nm). The size of synthesized nanoparticles, estimated from absorption spectrum, is about 2.2 nm. Thermal evaporation of DDA in a vacuum leads to the growth of InP nanoparticles up to ~3.2 nm with simultaneous vanishing of excitation peak in absorption spectra without luminescence degradation.

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