Influence of Amines and Alkanethiols on the Spectral and Luminescent Properties of InP@ZnS Colloidal Quantum Dots

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Abstract—It has been shown that the precursors (long-chain amines and alkanethiols) used in liquid-phase colloidal synthesis of InP@ZnS quantum dots exert a significant influence on their spectral and luminescent properties. It has been found that dodecylamine and 1-dodecanethiol facilitate obtaining the particles with a narrow luminescence band and a low quantum yield, whereas oleylamine, 1-octanethiol, and 1,6-hexanediethiol stimulate the formation of the quantum dots with broad and intense luminescence. Conditions have been found under which the narrowing of the emission band to 46.3 nm becomes possible.

Keywords: colloidal quantum dots, indium phosphide, liquid-phase synthesis, amines, alkanethiols, spectral and luminescent properties

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INTRODUCTION

In the modern world, much attention is paid to the creation of ecologically safe nanomaterials [1]. In this regard, of great interest are colloidal quantum dots (CQDs) of A\textsuperscript{III}B\textsuperscript{V} semiconductors, mainly of indium phosphide, which possess significantly lower toxicity than widespread CdSe [2, 3]. Indium phosphide has a rather narrow band gap (1.35 eV at 300 K [4]) and a large Bohr exciton radius (10.6 nm [5]), which permits CQDs of this composition to exhibit a stronger size effect than A\textsuperscript{II}B\textsuperscript{VI} CQDs.

One of the most promising methods of obtaining CQDs with specified spectral and luminescent properties is liquid-phase synthesis involving organometallic precursors. However, the high strength of the bond between In and P [6] complicates separation of nucleation and particle growth processes, which favors the formation of a large number of surface defects serving as centers for nonradiative recombination of electrons and holes. To obtain InP CQDs with efficient luminescence, it is necessary to passivate these centers, for example, by chemical modification of the surface of the particles or by building up around the particles of an additional shell of a wider-gap semiconductor, for example, ZnS.

In addition, the properties of CQDs are greatly influenced by the nature of the starting reagents. Various organic or inorganic salts can be used as the metal source: In(CH\textsubscript{3}COO)\textsubscript{3}, InCl\textsubscript{3}, (CH\textsubscript{3})\textsubscript{3}In. Numerous variants were proposed for a source of phosphorus. In various works, white [7] and yellow [8] phosphorus, phosphorus chloride (PCl\textsubscript{3}) [9], Na\textsubscript{2}P [10], gaseous phosphine [11–13] were used for this purpose, but the most widespread is tris(trimethylsilyl)phosphine (TTMSP), which favors the formation of particles sufficiently uniform in size [14–18]. However, this extremely reactive compound (like its closest analogs containing the P–Si bond [19, 20]) is expensive, toxic, and flammable; therefore, the work with this compound is possible only with taking special precautions.

Recently, tris(dimethylamino)phosphine (P(N(CH\textsubscript{3})\textsubscript{2})\textsubscript{3}, TDMAP) has been used as the precursor of phosphorus [21–23]. The use of this reagent permits substantial facilitation of the synthesis of InP CQDs, since it is much less expensive and less toxic than TTMSP. Using TDMAP and dodecylamine (DDA) as a coordinating solvent and a stabilizing ligand, InP [22] and InP@ZnS [23] CQDs were successfully synthesized. The core@shell particles formed in this case have intense luminescence (up to 50–70%), but they are characterized by rather broad emission spectra (with a width at half height of 68–73 nm [22] and 55–80 nm [23] for InP and InP@ZnS, respectively). In the presence of oleylamine (OA), InP@ZnS nanoparticles were obtained with a luminescence band width of 60–64 nm [24]. This is twice as large as for CdSe (about 30 nm) [5]. The broad luminescence bands indicate significant polydispersity of the particles due to the high bond strength in InP, which hampers the synthesis of monodisperse QDs due to difficulties in separating the stages of
nucleation and growth of the particles. It was shown in [25] that the length of the hydrocarbon chain of the amine molecule could affect the width of the luminescence band, but the values of the width were also found to be too large.

Among various sources of sulfur necessary for the formation of the ZnS shell, in our opinion, alkanethiols are the most promising. These compounds are readily soluble in a coordinating solvent and are more resistant to oxidation by air than conventionally used complexes of sulfur with trioctlyphosphine or amine, as well as (alkylsilyl)sulfide. In addition, a strong C–S bond provides a slow release of sulfur, which facilitates the creation of favorable conditions for controlling the growth of the shell.

This work is devoted to the study of the influence of the nature of long-chain amines (dodecylamine, tetradecylamine, hexadecylamine, and oleylamine) in the stabilizing shells, which are used to build up ZnS shells of alkanethiols (1-octanethiol, 1-dodecanethiol, and 1,6-hexanediethiol), on the spectral and luminescent properties of InP@ZnS CQDs in the course of liquid-phase colloidal synthesis.

EXPERIMENTAL

To synthesize InP@ZnS CQDs, the following reagents were used: indium(III) chloride (99.995%, Aldrich), zinc chloride (anhydrous, 98%, Sigma–Aldrich), DDA (98%, Aldrich), tetradeциамин (TDA, 95%, Aldrich), hexadecylamine (HDA, 90%, Aldrich), OA (80–90%, Acros), TDMAP (97%, Aldrich), 1-dodecanethiol (DDT, 98%, Aldrich), 1-octanethiol (OT, ≥98.5%, Aldrich), 1,6-hexanediethiol (HDT, ≥97%, Fluka), chloroform (99.5%, Aldrich), 1,6-hexanediethiol (HDT, ≥97%, Fluka), chloroform (99.5%, Sigma–Aldrich, with amylene content of 0.01–0.02%), and methanol (reagent grade, Khimmed).

The InP cores were obtained on the basis of the procedure reported in [24]. For this purpose, a mixture of InCl₃ (0.9 mmol), ZnCl₂ (0.9 mmol), and amine (15.2 mmol) was placed in a reaction vessel, degassed at 110°C for 40 min, after which the temperature of the mixture was raised to 220°C in an argon atmosphere, and the phosphorus precursor TDMAP (1.4 mmol) was added. In the presence of this reagent, the cores with an average diameter of 1.5 nm were formed within 30 s, and those 2.7 nm in diameter within 10 min. To build up the ZnS shell, the sulfur precursors (the corresponding alkanethiol or a mixture of thiols, 10.6 mmol) were introduced into the reaction mixture. Then the growth of the nuclei was stopped or occurred very slowly, and their size was estimated from the spectral data, using the expression reported in [26]. After that, the temperature in the reaction vessel was reduced to 200°C, and the mixture was held for 1–3 h. To complete the process, the mixture was rapidly cooled by feeding water into the jacket of the reaction vessel, and when the temperature decreased to 110°C, toluene (20 mL) was added into the reactor. For the subsequent use, the CQDs obtained were washed out with methanol (1 : 1 in volume), precipitated on a centrifuge (3000 rpm), dried, dispersed in chloroform, and filtered through PTFE membranes with a pore diameter of 450 nm.

The absorption spectra of the solutions studied were measured on a Shimadzu UV-3101PC spectrophotometer and an Ocean Optics HR–2000 fiber spectrometer. The luminescence spectra were recorded on an Ocean Optics USB2000–FLG fiber spectrofluorimeter at excitation with light of a wavelength of 400 nm.

The luminescence quantum yields (φ) were determined for dilute solutions of CQDs (with a concentration of particles ≈10⁻⁷ mol/L and an absorbance at the excitation wavelength below 0.1) against rhodamine 6G (with the quantum yield in water of 0.96 ± 0.02 [27]) with allowance for the refractive indices of the corresponding solvents [28]:

\[
\phi = 0.96 \frac{D_{\text{rh}}}{D_{\text{CQD}}} \frac{I_{\text{CQD}}}{I_{\text{rh}}} \left( \frac{n}{n_{\text{aq}}} \right)^2 
\]

where \(D_{\text{rh}}\) and \(D_{\text{CQD}}\) are the absorbances of an aqueous solution of rhodamine 6G and CQDs in an organic solvent, respectively, at a wavelength of 400 nm; \(I_{\text{rh}}\) and \(I_{\text{CQD}}\) are the areas of the luminescence bands of rhodamine 6G and CQDs, respectively; and \(n\) and \(n_{\text{aq}}\) are the refractive indices of the solvent and water, respectively.

RESULTS AND DISCUSSION

Influence of Amines

Figure 1 shows the changes in the absorption and luminescence spectra of InP@ZnS CQDs with an average core diameter of 2.7 nm in the course of the formation of the ZnS shell involving DDA (curves 1–6) and OA (curves 7–12). As a source of sulfur, DDT was used. In the absorption spectra of such particles, an excitonic peak is observed in the region of 550 nm, and in the luminescence spectra, a symmetrical band is observed with a maximum at 580–590 nm characteristic of the band–band mechanism. It follows from the figure that for CQDs obtained in the presence of DDA, the excitonic peak has a more pronounced shape (curves 1–3), whereas for the particles stabilized by OA, it looks blurred (curves 7–9). In addition, the luminescence bands of CQDs synthesized involving DDA are characterized by a smaller width (55 nm in 70 min after the introduction of DDT), and the position of the maximum in 70 min shifts to the red by 5 nm (curves 5 and 6), whereas with OA the position of the band does not change during this time, and its width is 66 nm.

Figure 2 shows the absorption and luminescence spectra of CQDs with a smaller average core diameter.