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On Stabilization of Colloidal Quantum Dots of Cadmium Selenide in the Presence of Octadecylphosphonic Acid

A. V. Nevidimov* and V. F. Razumov

Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia
**e-mail: nevidimovsasha@yandex.ru*

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Abstract—Classical molecular dynamics has been used to study the stabilization of colloidal quantum dots of CdSe with *n*-octadecylphosphonic acid molecules in combination with different auxiliary ligands, such as trioctylphosphine, trioctylphosphine oxide, and hexadecylamine. The effects of different ligands that may be formed due to interactions of *n*-octadecylphosphonic acid with CdO and Se in an initial mixture have been considered. It has been shown that, among these ligands, the stabilizing effect increases with a rise in the charge of a ligand per *n*-octadecyl chain. The role of the auxiliary ligands, e.g. octadecene that devoid of functional groups, has been studied.

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1. INTRODUCTION

One of the most common methods used for the synthesis of colloidal quantum dots (CQDs) with narrow size distributions (5–7%) is high-temperature colloidal synthesis [1–7]. The synthesis is carried out at a temperature of nearly 300°C in special mixed solvents that are liquid at this temperature. Initially, a mixture of trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO) was used for this purpose. TOP and TOPO molecules play the role of not only a solvent, but also precursors of components composing a quantum dot. For example, a TOP molecule forms a compound with a molecular structure of a chalcogene, while a TOPO molecule forms a complex with a metal:

$$\mathrm{TOP} + \mathrm{Se} = \mathrm{TOPSe}, \qquad (1)$$

$$\mathrm{TOPO} + \mathrm{CdO} = \mathrm{TOPO} \cdot \mathrm{CdO}. \qquad (2)$$

Mixing solutions containing chalcogene (1) and metal (2) leads to the formation of nanoparticles:

$$\mathrm{TOPSe} + \mathrm{TOPO} \cdot \mathrm{CdO} = \mathrm{CdSe} + 2\mathrm{TOPO}. \qquad (3)$$

In addition, TOP and TOPO molecules serve as stabilizing ligands, which cover particles and prevent them from coagulation. A substantial fraction of nanoparticle atoms is located on the surface. Surface atoms have a smaller number of neighbors than have atoms in bulk; therefore, they are, to a greater extent, subjected to the influence of different environmental agents, such as oxygen with which they interact as follows:

$$2\mathrm{CdSe} + 3\mathrm{O}_2 = 2\mathrm{CdSeO}_3. \qquad (4)$$

Oxidation via reaction (4) substantially deteriorates the luminescent properties of a nanoparticle [8, 9]. A molecule of a stabilizing ligand forms a lacking bond with a surface atom, thereby increasing its resistance to the action of oxygen. For example, TOP phosphorous coordinates a selenium atom, while TOPO oxygen coordinates a cadmium atom. The optical properties of nanoparticles contained in a mixture of initial solvents remain preserved for rather a long time. However, a mixed solvent, which is used for the synthesis and is liquid at 300°C, solidifies at room temperature. To make the further use of quantum dots (QDs) more convenient, it is necessary to replace the initial solvent by a solvent that is liquid at room temperature. Chloroform is commonly used for this purpose. Molecules of the high-boiling solvent are washed out by repeated dissolution in chloroform followed by precipitation of QDs with methanol. Therewith, the stabilizing ligand shell remains preserved to protect the nanoparticle surface. However, the protective efficiency of the shell decreases with time. As a result, the quantum yield of QD luminescence, which is primordially low, decreases still more. As has been found in [10], this is caused by two factors. First, TOP and TOPO ligands are easily washed out of a shell in the presence of a solvent. Second, the fraction of surface atoms coordinated by the ligands is small (0.26 for a 3.8-nm particle).

The stability of the optical properties may be improved by carrying out the synthesis in the presence of additional ligands, such as phosphonic acids, amines, or thiols. When CdSe quantum dots synthesized in the presence of TOPO and *n*-octadecylphosphonic acid (ODPA) are exposed in chloroform, their quantum yield even increases rather than decreases

Table 1. Initial parameters of the systems. Symbols A and B denote anionic residue of ODPA and anionic residue of its anhydride

System	Form ODPA/HDA	TOP	TOPO	ODPA	HDA
C1	CdA	53	53	30	–
C2	$Cd(HA)_2$	53	53	20	–
C3	H_2B	53	53	20	–
C4	$Cd(HB)_2$	53	53	10	–
C5	HA^-, RNH_3^+	53	53	20	20

[11]. The more efficient stabilizing effect of ODPA has failed to be explained with the use of simulation in [12]. ODPA molecules can be washed out of a shell with a solvent as well as TOP and TOPO molecules. Hence, an ODPA molecule is not bonded to the surface stronger that a TOPO molecule is in spite of the presence of two additional oxygen atoms. The more compact structure of ODPA molecules enables them to be more densely packed in the shell and coordinate neighboring cadmium atoms. At the same time, TOPO can coordinate only next nearest cadmium atom. However, this is, obviously, insufficient to exhaustively explain the stabilizing action of ODPA and the improvement the QD properties with time.

It has been experimentally shown [13] that ODPA may be present in the shell in one or several different ionic forms. This is reasonable, because the dissolution of basic cadmium oxide in dibasic ODPA at a high temperature may be accompanied by the following reactions:

$$RPO_3H_2 + CdO = RPO_3Cd + H_2O, \quad (5)$$

$$2RPO_3H_2 + CdO = Cd(RPO_3H)_2 + H_2O. \quad (6)$$

The ratio between the fractions of the salts formed via reaction (5) and (6) depends on the x = [ODPA] : [CdO] ratio. When $x \le 1$, the product will contain only neutral salt. At $1 < x < 2$, the product will comprise a mixture of neutral and acidic salts. At $x = 2$, only acidic salt will be formed. At $x > 2$, the reaction will yield a mixture of acidic salt and neutral ODPA acid. A subsequent interaction of cadmium compounds with TOPSe complex will result in the formation of more complex compounds in the solution. This will be considered in greater detail below. Now, a simple fact is worth noting: the qualitative and quantitative composition of mixed ligands will depend on the number ratios of ODPA molecules and cadmium and selenium atoms in initial mixtures. When experimenters reveal that ODPA is distributed in a ligand shell over some forms 1, 2, ..., N in a certain ratio, it must be recognized that this is valid only for specific synthesis conditions. If the initial concentrations of the reagents are changed, the forms of ODPA compounds per se and the ratio between them will be different.

In this work, we shall investigate the stabilizing effects of different forms of ODPA. As will be shown below, chemical interactions in the initial mixtures may transform ODPA into simple salts via reactions (5) and (6), anhydride, and its acidic cadmium salt. A question of whether a neutral salt of the anhydride may be formed is debatable; therefore, effect of this salt will not be considered.

As ODPA stabilizes CdSe QDs so efficiently, it seems like TOPO should be avoided entirely. However, particles are not formed at all in this case [14]. It is obvious that specific forms of ODPA compounds, which are formed in the system at a large excess of ODPA with respect to CdO, are responsible for this. Therefore, a detailed analysis of the ODPA interaction with cadmium and selenium will enable us to explain the reason for suppressing the formation of nanoparticles. Moreover, it is of importance to explain, why the addition of small amounts of neutral components, such as octadecene, to ODPA gives rise to the formation of stable nanoparticles, even in the absence of TOPO. A possible action of amines in combination with ODPA is also of interest, because they may interact with each other at different stages of the synthesis. For example, if an amine interacts with the acid at an initial stage via scheme

$$R^*NH_2 + RPO_3H_2 = R^*NH_3^+ + RPO_3H^-, \quad (7)$$

this will inevitably affect the reaction products of the acid and cadmium.

2. MOLECULAR MODELS AND PARAMETERS OF SIMULATION

All calculations were performed using the NAMD 2.10 software package [15] with the Lomonosov supercomputer and at the computation center of the Institute of Problems of Chemical Physics, Russian Academy of Sciences [16]. In each case, a simulation cell had sizes of nearly $12 \times 12 \times 12$ nm^3. A spherical CdSe QD 3.8 nm in diameter was placed into the center of the cell. This quantum dot was composed of 499 cadmium atoms and 499 selenium atoms, as had been described in [10]. The preset numbers of ligand molecules (TOP, TOPO, ODPA, and hexadecylamine (HDA), see Table 1) were uniformly distributed around the QD with the use of a specially developed program [17]. The rest of the cell space was filled with chloroform molecules. Initially, the energy of the constructed systems was minimized for 0.1 ns; then, the calculation was performed for 20 ns.

The Newton equation of motion was integrated using the velocity Verlet algorithm with an integration step of 1 fs. The isobaric–isothermal *NPT*-ensemble and periodic boundary conditions were used for all calculations. A pressure of 1 atm and a temperature of 298.15 K were maintained with the use of Berendsen barostat and the velocity-reassigning procedure. The

Table 2. Charges of atoms and groups

Atom	q, e^-	Atom	q, e^-	Atom, group	q, e^-
Cd	+1.18	O in X–O–Y	–0.57	P in TOP, TOPO	+0.78
Se	–1.18	O in X=O, X–O$^-$	–0.78	$\Sigma(RNH_3^+)$	+0.59
H in H–O	+0.21	P in H_2A	+1.5	$\Sigma(HA^-)$, $\Sigma(HB^-)$	–0.59
H in RNH_2	+0.4	P in HA^-	+1.33	$\Sigma(A^{2-})$	–1.18
H in RNH_3^+	+0.3	P in A^{2-}	+1.16	C in $CHCl_3$	+0.179
N in RNH_2	–0.8	P in H_2B	+1.425	H in $CHCl_3$	+0.082
N in RNH_3^+	–0.31	P in HB^-	+1.34	Cl in $CHCl_3$	–0.087

VMD software package [18] was used for the visualization and analysis of the systems. The CHARMM27 force field was applied to describe all molecules. The parameters of Cd and Se atoms were taken from [19], while model presented in [20] was used for the solvent (chloroform). The charges of the atoms of ligand functional groups are listed in Table 2.

3. RESULTS AND DISCUSSION

The products that may be formed as a result of ODPA interaction with cadmium oxide and amines at the first stage of the synthesis via reactions (5)–(7) have been considered above. Now, we shall consider the ligands that may be formed subsequently upon the addition of selenium and the effects of these ligands on a nanoparticle. Let us denote the anionic residue of ODPA and the anionic residue of its anhydride as A and B, respectively. Then, the acid and anhydride will have formulas H_2A and H_2B, respectively.

3.1. Neutral Salt of Octadecylphosphonic Acid

If neutral CdA salt alone is formed in the system (at $x = 1$), its possible reaction with TOPSe may be written as follows:

$$2CdA + TOPSe = CdSe + CdB + TOPO. \qquad (8)$$

One CdB ligand containing one excess cadmium atom is formed per CdSe molecule. Immediately after being formed, a nanoparticle will be covered with CdB, TOPO, and, possibly, CdA and TOP ligands. Therewith, the number of CdB molecules will be equal to the number of CdSe molecules contained in the nanoparticle. It is of importance to clarify whether CdB molecules may be detached from the nanoparticle surface under the synthesis conditions, i.e., at 300°C in the mixed high-boiling solvents. Computer simulation of a system, in which a chemical reaction occurs, must be performed using quantum-chemical methods. However, this seems to be rather difficult for such a complex system. Therefore, the aforementioned question can hardly be unambiguously answered. To begin with, we may consider a simpler system and answer the question of whether a ligand molecule containing a cadmium cation may be detached from a nanoparticle surface in chloroform at room temperature. CdA or CdB may be taken as a ligand molecule, because their behavior will, most probably, be similar.

Let us consider the C1 system, in which the shell consists of a mixture of TOP, TOPO, and CdA ligands (Table 1). For this and other systems, we deliberately provide the presence of an excess number of ligands in order to verify the possibility of their detachment from the surface. The monitoring of the C1 system for 20 ns has shown the following. All CdA molecules have remained in the cell, while some TOP and TOPO molecules have passed to the solvent. All excess cadmium cations have been embedded into the structure of the nanoparticle (Fig. 1). Now, we shall determine the sites of their embedding. Let us consider an atom–atom distribution function for Cd–Se and Cd–Cd pairs of atoms in the C1 system (Fig. 2a). For comparison, a similar diagram has been plotted for an initial CdSe nanoparticle free of excess cadmium cations (Fig. 2b). Attention is attracted by a small peak in the Cd–Cd radial-distribution function at r = 2.7 Å, which is absent in the latter figure. Excess cadmium cations are embedded at a short distance from other cadmium cations. The short distances between Cd atoms indicate that all of them are located at the nanoparticle surface, with the number of short Cd–Cd bonds being almost equal to the number of excess cadmium atoms (Fig. 3). Hence, excess cadmium cations are located only on the surface and cannot penetrate into the nanoparticle bulk. From this fact the following important conclusion may be inferred: the maximum number of CdA molecules of the ligand is equal to the maximum number of excess cadmium cations that the nanoparticle surface can accommodate. The latter value may be roughly estimated by equating it to the number of the surface selenium atoms. As is known the fraction of the surface atoms decreases with an increase in the size of a nanoparticle. Therefore, if the detachment of a CdA (CdB) molecule from the nanoparticle surface is hin-

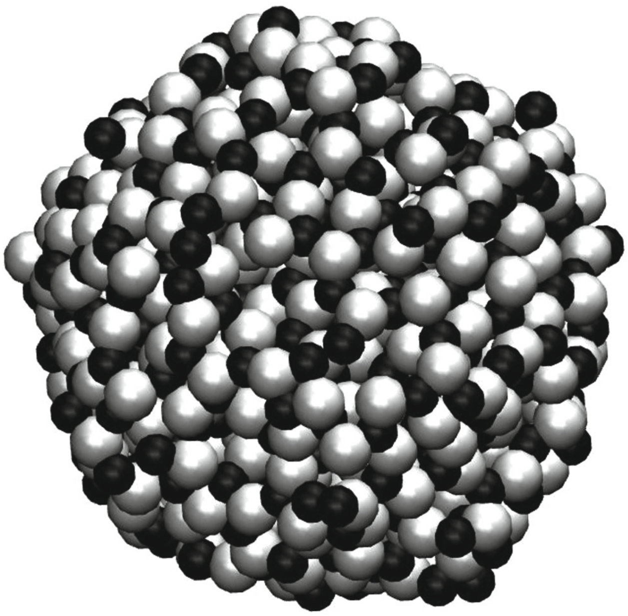

Fig. 1. CdSe nanoparticle in C1 system 20 ns after the onset of simulation. Black and white symbols refer to cadmium and selenium, respectively.

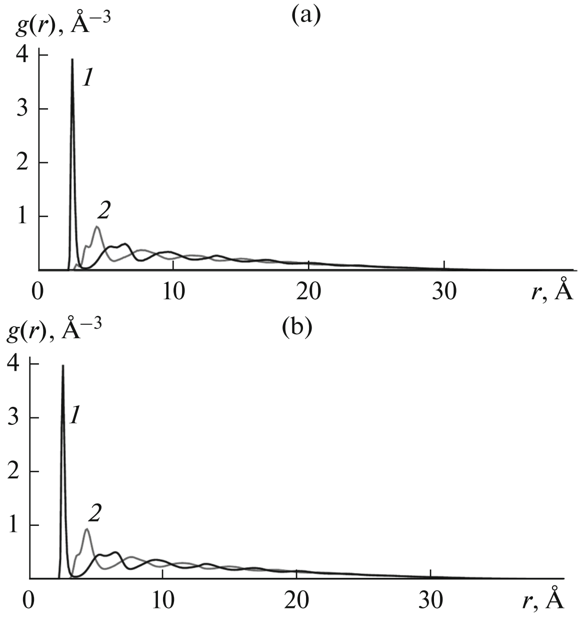

Fig. 2. Pair correlation functions for (*1*) Cd–Se and (*2*) Cd–Cd in C1 system (a) in 20 ns and (b) at the onset of simulation.

dered under the synthesis conditions, the growth of nanoparticles may also be suppressed.

3.2. Acidic Salt of Octadecylphosphonic Acid

Now, we shall consider another limiting case, in which the initial ratio is $x = 2$. In this case, the dissolution of cadmium in ODPA yields its acidic salt, $Cd(HA)_2$. This substance may interact with TOPSe complex according to the following scheme:

$$Cd(HA)_2 + TOPSe = CdSe + H_2B + TOPO. \quad (9)$$

Then, one ODPA anhydride molecule and one TOPO molecule are formed per CdSe molecule. In addition to these ligands, the shell may contain excess TOP and intact $Cd(HA)_2$. However, in the course of the reaction, its fraction must decrease. As in the previous case, let us clarify whether H_2B and $Cd(HA)_2$ ligands may be detached from the surface under the action of the external solvent.

The C2 system contains $Cd(HA)_2$, TOP, and TOPO ligands, while the C3 system—H_2B, TOP, and TOPO ligands. Under the conditions of surface deficiency, excess ligands must seek to escape from the shell. This is the case for TOP, TOPO, and H_2B molecules. All $Cd(HA)_2$ molecules have remained in the shell. A molecule of the acidic salt of ODPA contains one excess cadmium atom. An analogous analysis of the distribution of excess cadmium cations has shown that they are also embedded into the structure of the nanoparticle and are located on its surface. However, in contrast to the neutral salt, in the acidic one, two anionic ODPA residues correspond to one excess cadmium atom. Moreover, the content of the acidic salt gradually decreases in the system; therefore, the amount of excess cadmium atoms gradually decreases, and the growth of nanoparticles is not hindered. In the

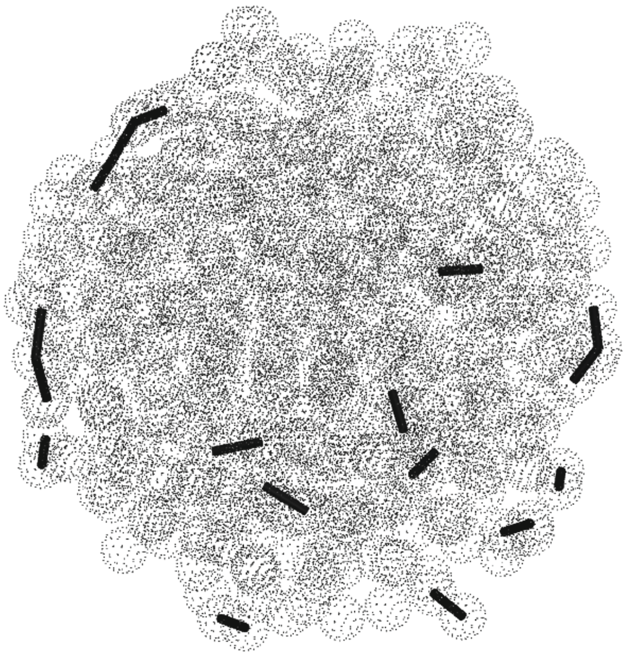

Fig. 3. CdSe nanoparticle in C1 system 20 ns after the onset of simulation. Lines connect Cd atoms located at distances of no longer than 3.3 nm.

presence of a sufficient amount of TOPSe, the acidic salt will be entirely consumed, and H_2B, TOP, and TOPO ligands will remain in the ligand shell, with all these ligands being easily washed out with chloroform. Therefore, the luminescent characteristics of such particles must be gradually deteriorated, as it takes place for the synthesis in a TOP–TOPO mixture. Under the deficiency of selenium, part of $Cd(HA)_2$ will remain in the ligand shell of the nanoparticle to protect it.

3.3. Mixture of Neutral and Acidic Salts of Octadecylphosphonic Acid

Commonly, the synthesis is performed taking ratio x in a range of from 1 to 2. Under these conditions, the dissolution of cadmium oxide in ODPA yields a mixture of CdA and $Cd(HA)_2$ salts. The higher x, the larger the fraction of the acidic salt. The $x = 4 : 3$ ratio is of interest. In this case, the ratio between the neutral and acidic salts is equal to 2 : 1:

$$4H_2A + 3CdO = 2CdA + Cd(HA)_2 + 3H_2O. \quad (10)$$

The summation of Eqs. (10), (8), and (9) yields the total equation, in which the reaction products contain CdB and H_2B in a ratio of 1 : 1. As is known, dibasic acids may interact with their neutral salts to yield an acidic salt as follows:

$$CdB + H_2B = Cd(HB)_2. \quad (11)$$

Taking into account Eq. (11), the total equation for the formation of nanoparticles may be written as

$$\begin{aligned} &4H_2A + 3CdO + 2TOPSe \\ &= 2CdSe + 2TOPO + Cd(HB)_2 + 3H_2O. \end{aligned} \quad (12)$$

At $x = 4 : 3$, only $Cd(HB)_2$ ligand is formed in the system. When $1 < x < 4 : 3$, CdB will be present in the mixture together with the former ligand; at $4 : 3 < x < 2$, H_2B will be formed in the mixture. As in the previous case, this consideration is valid at a sufficient amount of selenium; i.e., provided that the Cd : Se ratio is not higher than 3 : 2.

If Cd : Se > 3 : 2, seven ODPA derivatives will always be present in the system. The qualitative and quantitative compositions of this mixture are rather diverse, and the complete analysis is out of the scope of this article. Omitting the detailed calculations, let us present an interesting mixture of ligands, when Cd : Se = 2 and $x = 1.5$:

$$\begin{aligned} &6H_2A + 4CdO + 2TOPSe \\ &= 2CdSe + 2TOPO + Cd(HB)_2 \\ &\quad + Cd(HA)_2 + 4H_2O. \end{aligned} \quad (13)$$

At these parameters, the shell contains acidic salts of ODPA and of its anhydride, but when $x > 1.5$, ODPA or its anhydride themselves will be present together with them. Compositions close to these ratios were used in some experimental works [19].

It can be seen that, at all x values within a range from 1 to 2, and any Cd : Se ratios, $Cd(HB)_2$ is present among the ligands. This molecule contains one cadmium atom per four octadecane chains. Most likely, this molecule will be weaker bonded to the nanoparticle surface and may be detached from it under the action solvents. In order to verify this assumption, let us consider the C4 system, which contains $Cd(HB)_2$, TOP, and TOPO ligands. The monitoring of this system has shown that all $Cd(HB)_2$ molecules remain preserved in the shell, while TOP and TOPO molecules are gradually washed out of it. In the C4 system, all excess cadmium cations have also been located on the surface. Owing to the fact that their number per octadecene chain is four times lower than that in the case of CdA, ligands of the C4 system must have a lower inhibiting effect on nanoparticle growth than CdA has. At the same time, the presence of cadmium cation enables $Cd(HB)_2$ molecule to resist the washing-out action of the solvent and to protect the nanoparticle surface from oxidation.

3.4. Octadecylphosphonic Acid and Hexadecylamine

When ODPA is used in combination with TOP and TOPO, two limiting cases are possible. If ratio x is low, the ligand shell contains many CdA and CdB molecules, which interact with the surface so strongly that may hinder nanoparticle growth. If x is high, the shell contains H_2B molecules, which are gradually washed out in the course of nanoparticle storage. Therefore, the necessity arises to select some optimum x and a corresponding Cd : Se ratio in a manner such that these parameters would provide a balance between the "comfortable" growth and efficient post-synthesis stabilization of nanoparticles. Another approach to the stabilization of a nanoparticle surface is the use of additional ligands other than TOP and TOPO, e.g., HDA. The key difference is the interaction between the amine and the acid with the formation of the ionic forms indicated in Eq. (7). The ionic form of ODPA, which may, in the new notations, be written as HA^-, contains no cadmium cation. The cationic form of the amine is present in the shell instead of cadmium. Therefore, the amount of such ligands is limited by the packing density alone. Let us verify whether the ionic forms of ODPA and HDA are strongly retained in the shell in the presence of a solvent.

The C5 system contains ionic forms of ODPA and HDA molecules, as well as TOP and TOPO molecules. TOP and TOPO molecules were used to create excess ligands. The monitoring of this system has shown that ODPA and HDA molecules do not leave the ligand shell, while TOP and TOPO molecules do leave. The detailed study of the nanoparticle structure has shown that it almost corresponds to the structure of a nanoparticle covered with a mixture of TOP and TOPO. The peak corresponding to the short Cd–Cd

Table 3. Parameters of final systems. Compositions and dipole moments μ

System	Form ODPA/HDA	TOP	TOPO	ODPA	HDA	μ, a. u.
C1	CdA	27	51	30	–	185
C2	$Cd(HA)_2$	14	52	20	–	80
C3	H_2B	26	52	15	–	41
C4	$Cd(HB)_2$	12	50	10	–	50
C5	HA^-/RNH_3^+	18	50	20	20	145
D1	–	–	–	–	–	21
D2	–	37	68	–	–	33
D3	H_2A	23	49	21	–	41
D4	RNH_2	12	53	–	30	70

distances is absent in the plot of the radial-distribution function. There are no Cd atoms adjacent to each other. Hence, the fraction of the aforementioned ionic forms in the shell may reach 100%.

3.5. Nanoparticle Dipole Moment

The observation of the C1–C5 systems has shown that CdA, $Cd(HA)_2$, $Cd(HB)_2$, HA^-, and $R^*NH_3^+$ ligands do not pass from the shell into chloroform. This indicates their strong bonding to the nanoparticle surface. However, this fact does not enable us to determine the relative strength of bonding these ligands to the surface. As has been noted in [21], the presence of ligands around a nanoparticle affects its dipole moment. Indeed, if there are no ligands around a small particle, its ions are poorly ordered; therefore, the dipole moment is low. A ligand shell may be considered as an electric field surrounding a nanoparticle. The stronger the field, the stronger the ions must be ordered in the nanoparticle and the higher its dipole moment must be.

For comparison, dipole moments were calculated for CdSe nanoparticles in the C1–C5 systems and in four more systems. The D1 system is represented by an initial CdSe nanoparticle containing 499 Cd and 499 Se atoms. The D2 system is the nanoparticle with a shell composed of 37 TOP molecules and 68 TOPO molecules [10]. The D3 system is the nanoparticle with a shell composed of 30 TOP molecules, 49 TOPO molecules, and 24 H_2A molecules [12]. The D4 system is the nanoparticle with a shell composed 12 TOP molecules, 53 TOPO molecules, and 30 neutral HDA molecules [12]. The calculation was performed by the following standard formula:

$$\mu = \left\langle \left\| \sum_i q_i \mathbf{r}_i \right\| \right\rangle, \tag{14}$$

where q_i denotes charges, $\mathbf{r}_i$ denotes radius vectors of atoms, and broken brackets $\langle ... \rangle$ denote averaging over 1000 instantaneous configurations.

The calculated dipole moments are listed in Table 3. It may be inferred from the calculation results that the presence of the ligands affects the nanoparticle structure indeed. The nanoparticle free of a ligand environment is poorly ordered, and its dipole moment is lowest. In the environment of TOP and TOPO molecules, atoms of the nanoparticle are somewhat ordered, and its dipole moment somewhat increases. Partial replacement of the ligand shell molecules by ODPA or its anhydride increases the dipole moment a little more. Hence, ODPA and its anhydride interact more strongly with the nanoparticle than TOP and TOPO do. An analogous speculation may be performed concerning other ligands. Of course, it is not quite correct to directly compare the bonding strengths of ligands in this way, because the systems contain different numbers of ligand molecules in their shells. However, the general tendency is quite clear. Among different derivatives of ODPA, CdA ligand is bonded stronger than the others, while H_2A and H_2B ligands are bonded weaker than all others. An excess amount of CdA may inhibit nanoparticle growth. If a shell consists of only TOP, TOPO, H_2A, and H_2B ligands, its protective properties are poor because all molecules of such ligand shell may be washed out with a solvent. Therefore, it is necessary to find an optimum balance of starting ODPA : Cd and Cd : Se ratios, which govern the final forms of ODPA in a ligand shell. As follows from Table 3, the bonding strength of RPO_3H^-/RNH_3^+ ligands is comparable with that of CdA. In contrast to CdA they do not incorporate excess cadmium cations into a nanoparticle. Therefore, their content may reach 100%. For the same reason, they do not inhibit nanoparticle growth in the course of the synthesis. Hence, the use of such mixed ligands may be considered to be promising from the practical point of view.

3.6. Octadecylphosphonic Acid without Additives or with Neutral Additives

It has been experimentally found that nanoparticles are not formed in the presence of ODPA alone [14]. At the same time, the incorporation of octadecene molecules devoid of functional groups into the system facilitates the formation and stabilization of the particles. Both of these experimental facts seem, at first sight, to be mysterious. However, they may be explained on the basis of the aforementioned results.

As has been mentioned above, being dissolved in ODPA, CdO forms neutral salt, CdA, and acidic salt, $Cd(HA)_2$. The coordination number of cadmium cation is 4. Hence, in addition to anionic residues of ODPA, its coordination sphere contains neutral molecules. If the synthesis is performed in the presence of TOPO, they are TOPO molecules. In the case of octadecene, they are octadecene molecules. Although the latter has no functional groups, it will just fill the free space surrounding cadmium cations. TOPO ligands and, all the more, octadecene are easily detached from the nanoparticle surface, and it is reasonable to assume that their bonds with individual cadmium cations are also easy to rupture. The site left vacant may be occupied by TOPSe complex; in this case, reaction (3) may occur to yield CdSe.

If there are no ligands except for ODPA, the dissolution of CdO will result in the formation of $Cd(HA)_2$ acidic salt. In this case, cadmium cation will be surrounded by two H_2A molecules in addition to two anionic residues. It may be suggested that, at a high temperature, the interaction of HA^- anion with H_2A molecule followed by water elimination may take place:

$$HA^- + H_2A = HB^- + H_2O. \tag{15}$$

In this case, the cadmium cation will be surrounded by two anionic residues HB^-; other molecules are absent in the environment. As has been found for the C4 system, HB^- anions are strongly bonded to the surface. It may be supposed that the strong bond is formed near a cadmium cation. Since other molecules are absent in the environment of a cadmium cation and HB^- is strongly bonded to it, TOPSe complex cannot come to Cd, and particles do not grow.

4. CONCLUSIONS

ODPA can exhibit the properties of both a weak and a strong ligand when stabilizing cadmium selenide quantum dots. If it has the form of neutral H_2A or H_2B molecules, its stabilizing effect is weak and, similarly to TOP and TOPO, ODPA will gradually pass from the shell into a solution. Ionic forms of ODPA interact with the surface markedly stronger than the neutral forms do; therefore, they more efficiently protect the surface of the CQDs. However, some forms (CdA and CdB) interact so strongly that they may hinder the growth of nanoparticles because of the large number of excess cadmium cations present on their surface. When ligands in the form of acidic salts of ODPA are formed in the shell, then, on the one hand, they do not inhibit the particle growth, and, on the other hand, they ensure efficient stabilization. However, this requires the accurate selection of the ratios between the initial components of a reaction mixture. The ODPA : Cd ratio must be close to 1.5.

Any ODPA derivative containing Cd atoms adds these atoms to the structure of a nanoparticle embedding them into the surface. Since the surface cannot accommodate too many excess Cd cations, the fraction of cadmium-containing ODPA ligands in the shell cannot reach large values, thereby limiting the protective properties of ODPA. The use of amines in combination with ODPA makes it possible to avoid this circumstance, while strong bonding of ligands to the surface takes place under these conditions. In this case, the fraction of protected atoms of the CQD surface may reach 100%.

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