

Theoretical investigation of CdSe clusters: influence of solvent and ligand on nanocrystals

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Received: 1 June 2009 / Accepted: 28 June 2009 / Published online: 28 July 2009
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Abstract Based on experimental zinc blende and wurtzite models of CdSe nanocrystals, four clusters of CdSe, seven Se-Cd-ligand structures, and their characters are studied at DFT/B3LYP/Lan12dz theoretical level. Cd_3Se_3 , $(\text{Cd}_3\text{Se}_3)_2$ and $(\text{Cd}_3\text{Se}_3)_3$ clusters which have a ring with six atoms are similar to wurtzite structures, Cd_4Se_4 have resemblant conformation with zinc blende for they are all composed of tetrahedron. Calculated Raman spectra of Cd_3Se_3 , Cd_4Se_4 , $(\text{Cd}_3\text{Se}_3)_2$ and $(\text{Cd}_3\text{Se}_3)_3$ are about 175 cm^{-1} which is consistent with the experimental result. Then, through investigation of Se-Cd-ligand clusters, we find that all Se-Cd-ligand structures have similar characters because main influence of ligands on nanocrystals comes from thiol. Finally, we testify that both solvent and ligand make absorption peaks shift to blue, compared with those in gas phase and without ligand. Under these conditions, calculated data of four clusters are almost identical with the absorption peaks of CdSe nanocrystals. Besides, we also prove that the absorption peaks of four clusters are the transitions from HOMO to LUMO or from d to p orbitals. And HOMO-LUMO gaps reduce in order of Cd_3Se_3 , $(\text{Cd}_3\text{Se}_3)_2$ and $(\text{Cd}_3\text{Se}_3)_3$, which is induced by the quantum size effect.

Keywords Absorption peaks · CdSe · Raman spectra · TDDFT

Introduction

During the past two decades, semiconductor nanomaterials have attracted much attention not only for their variety of

new intriguing physical and chemical properties but also for their extensive applications [1–4]. II-VI semiconductor materials are particularly interesting and have been the focus of many experimental and theoretical investigations in recent years such as CdS [5], CdTe [6], ZnS [7], HgTe [8] and so on. This kind of material has wide-ranging applications because of their specific qualities. For example, these semiconductor materials were used as catalysts, solar cells, luminescent devices etc.

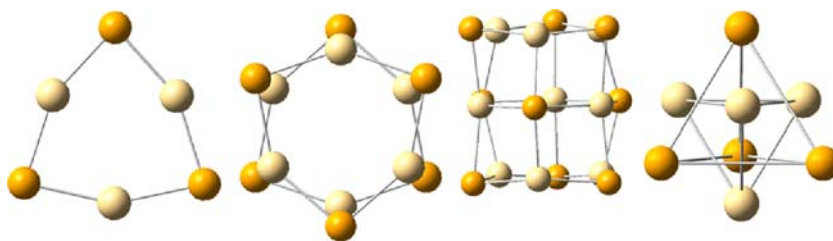
For CdSe structure, there were also many papers reporting its structures and characters. In 2003, Sarkar and Springborg, using LCAO-DFT-LDA method, studied Cd_mSe_n clusters with $n + m$ up to 200 [9]. In the same year, Cd_nSe_n ($n=17, 26$ and 38) clusters were obtained with *ab initio* [10]. Simultaneously many other conformations were reported and their corresponding characters are investigated both in experiment and theory [11–16]. Lately, Cd_2Se_2 was discussed with many different ligands [17], making the calculation closer to the condition of experiment. Namely, the calculated results are nearer to the experimental data. It is clear that many structures have been found and many methods have been used to investigate CdSe clusters in theory, and many results which were important for experiment were gained. However, there is no paper reporting the absorption spectra and Raman spectra which are the crucial characters of the CdSe nanocrystals. Moreover, the effect of ligand is unknown to us now. In this paper, we studied in detail the absorption and Raman spectra of CdSe structures and explored the influence of solvent and ligands on the characters of CdSe nanocrystals.

Calculation methods

Conformations and characters of Cd_3Se_3 , Cd_4Se_4 , $(\text{Cd}_3\text{Se}_3)_2$ and $(\text{Cd}_3\text{Se}_3)_3$ along with Se-Cd-ligand struc-

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Fig. 1 The conformation of Cd_3Se_3 , $(\text{Cd}_3\text{Se}_3)_2$, $(\text{Cd}_3\text{Se}_3)_3$ and Cd_4Se_4 molecules



tures were studied at DFT/B3LYP level with Gaussian03 package [18]. Basis set (Lanl2dz) was adapted to both Se and Cd atoms. Under this basis set, the outermost valence electrons $4s^2 4p^4 3s^2 3p^6 3d^{10}$ for Se, $5s^2 4s^2 4p^6 4d^{10}$ for Cd were described and their core electrons were not taken into account. Molecular orbital (MO) figures were generated using GaussView program. The absorption spectra were obtained with time-dependent DFT (TDDFT) at the same theoretical level with the optimization. In our paper, there are two kinds of calculated conditions for the absorption spectra. The first one is in gas phase which is default using TDDFT method to calculate the absorption spectra. The other one chooses water as a solvent in order to simulate the aqueous phase synthesis. As to this kind of TDDFT calculation, Scrf = (solvent = water) must be added to get absorption spectra. The permittivity of water in our paper is 78.39 ($\epsilon=78.39$). Finally, in order to gain the Raman spectra, Freq=Raman was added during the frequency calculation since Raman spectra were not automatically calculated with the DFT method generally speaking.

Results and discussion

Though CdSe semiconductor material has been synthesized and investigated in experiment, and some small CdSe clusters had been calculated using many methods in theory, comparison of the experiment and theory has not been established yet. The influence of solvent and ligand was always ignored. In the current work, on the basis of experimental zinc blende and wurtzite structures of CdSe nanocrystals, four new structures were reported first; then, through considering integration effect of solvent and ligand, calculated Raman and absorption spectra of CdSe clusters

were rational, compared with data of the experiment and quantum size effect.

Characters and modellings of CdSe clusters

Four structures Cd_3Se_3 , Cd_4Se_4 , $(\text{Cd}_3\text{Se}_3)_2$ and $(\text{Cd}_3\text{Se}_3)_3$ were depicted in Fig. 1 and their corresponding parameters were listed in Table 1. All these structure are stable in theory with the positive lowest vibrational frequencies. It is well-known that familiar structures of CdSe nanocrystals are zinc blende and wurtzite structures which take tetrahedron and hexagon as the units, respectively. In this paper, Cd_3Se_3 have hexagons, and Cd_4Se_4 is composed of tetrahedron. $(\text{Cd}_3\text{Se}_3)_2$ and $(\text{Cd}_3\text{Se}_3)_3$ are the simplest structures which are formed with hexagons. Thus, our structures should have similar characters as experimental zinc blende or wurtzite structures, though their sizes are much smaller than experimental CdSe nanocrystals. We also optimize rings with four and eight atoms (quadrangle and octagon) which have the negative lowest vibrational frequencies, showing their instability. Bond lengths of Cd_3Se_3 structure are about 2.596 Å. The distances between Cd and Cd atoms are different with those among Se and Se atoms. For $(\text{Cd}_3\text{Se}_3)_2$ molecule, its two hexagons have the same bond length 2.700 Å. The bond lengths between two layers are 2.865 Å which is longer than those in rings. $(\text{Cd}_3\text{Se}_3)_3$ molecule (D_{3H}) is composed of three rings. Bond lengths of the first and the third hexagons are equal (2.682 Å), but the middle layer has a different one (2.836 Å). Obviously, the middle layer has a longer bond length than those of two end rings. This testifies that it is difficult or impossible to form nanotube for CdSe nanocrystals because there is strong tensile force among hexagons. It can also be seen from the figure, except the middle ring of $(\text{Cd}_3\text{Se}_3)_3$

Table 1 Total energies (in a.u.), the lowest vibrational frequencies (cm^{-1}), the HOMO-LUMO gaps (in eV), symmetries, the states, compositions, absorbed wavelength (λ nm) and absorbed wavelength in water for Cd_3Se_3 , $(\text{Cd}_3\text{Se}_3)_2$, $(\text{Cd}_3\text{Se}_3)_3$ and Cd_4Se_4 molecules

structures	Energies	Freq	H-L	Symm	States	Compositions	λ	$\lambda(\text{W})$
Cd_3Se_3	-172.0647	45	3.24	C_1	1	27 -> 28	507	336
$(\text{Cd}_3\text{Se}_3)_2$	-344.2235	44	3.16	D_{3D}	1	53 -> 55	499	365
$(\text{Cd}_3\text{Se}_3)_3$	-516.3730	42	2.88	D_{3H}	1	81 -> 82	530	387
Cd_4Se_4	-229.4352	71	2.94	C_1	1	36 -> 37	542	346

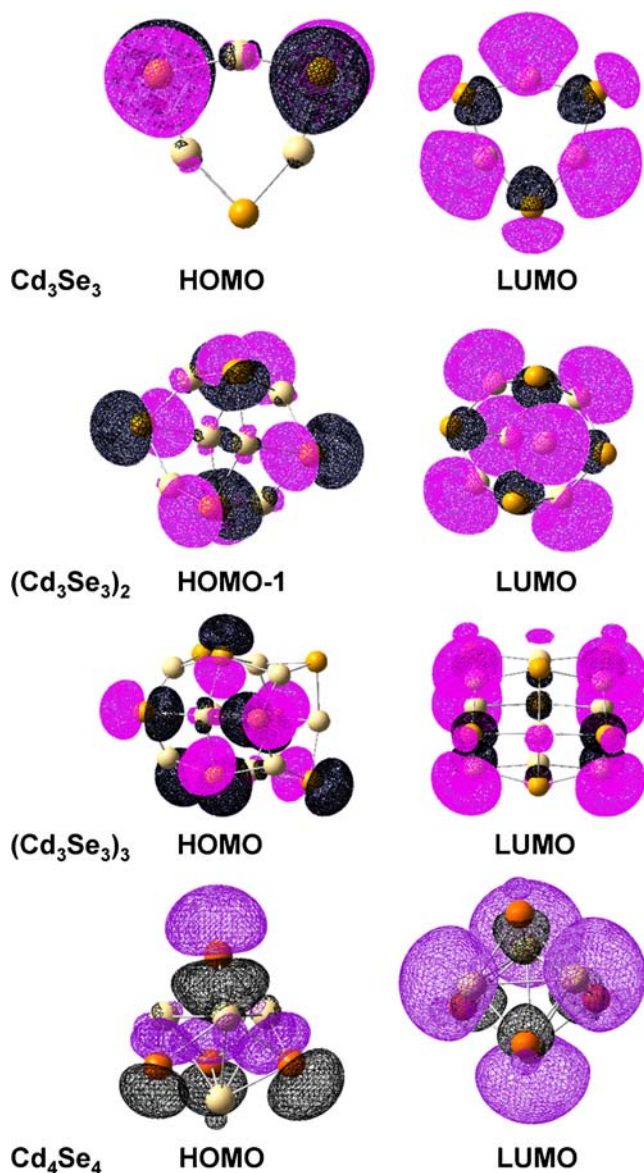


Fig. 2 Molecular orbital figures for Cd_3Se_3 , $(\text{Cd}_3\text{Se}_3)_2$, $(\text{Cd}_3\text{Se}_3)_3$ and Cd_4Se_4 molecules

molecule is in plane one for two end rings have the same tension to it, the other rings in $(\text{Cd}_3\text{Se}_3)_2$ and $(\text{Cd}_3\text{Se}_3)_3$ molecules are not planar and they change into dentate structures. In a word, Cd_3Se_3 , $(\text{Cd}_3\text{Se}_3)_2$ and $(\text{Cd}_3\text{Se}_3)_3$ have dentate hexagons, so they are similar to wurtzite structures. As for Cd_4Se_4 structure, it almost has the same bond lengths 2.780 \AA , *i.e.* we can consider it as regular tetrahedron. One Cd atom forms a tetrahedron with its closest three Se atoms, and vice versa. Therefore, Cd_4Se_4 structure is the smallest unit of zinc blende structure. Moreover, we believe that Cd_3Se_3 and Cd_4Se_4 structure are significant for the future theoretical calculation because big clusters can be optimized along them. And they are also more useful for the experiment since

they may be the small units of many experimental nanocrystals.

HOMO-LUMO gaps of conductor are less than 1 eV, insulator has higher gaps than 6 eV, and gaps of semiconductor belong to this scope (1 ~ 6 eV) in general. Seen from Table 1, HOMO-LUMO gaps of Cd_3Se_3 (3.24 eV), Cd_4Se_4 (2.94 eV), $(\text{Cd}_3\text{Se}_3)_2$ (3.16 eV) and $(\text{Cd}_3\text{Se}_3)_3$ (2.88 eV) structures display that they are semiconductor. In experiment, CdSe nanocrystals are also semiconductor materials [19]. Clearly, the theoretical conclusion is identical with the experiment result. Besides, with the increasing of the number of atoms, HOMO-LUMO gaps of (Cd_3Se_3) , $(\text{Cd}_3\text{Se}_3)_2$ and $(\text{Cd}_3\text{Se}_3)_3$ become narrow (3.24, 3.16 and 2.88 eV). Namely, through controlling the size of CdSe nanocrystals, we can achieve adjustment of the bandwidth. This conclusion is also identical with the experimental phenomenon of CdSe nanocrystals (quantum size effect), which illuminates that our method is fit to calculate CdSe clusters. And we will use this method to research other characters of CdSe structures.

Absorption spectra in solvent and gas phase were calculated using TDDFT which is appropriate to estimate absorption spectra of II-VI semiconductor materials [10, 14]. As to $(\text{Cd}_3\text{Se}_3)_2$ molecule, its HOMO and HOMO-1 are two degenerate orbitals. So the first states of four structures are the transitions from HOMO to LUMO. Firstly, we calculate the absorption peaks of four clusters without solvent and find the wavelengths of them are higher than those of experimental nanocrystals. Then, considering the condition of experiment, we add water as solvent and calculate their absorption peaks. Seen in Table 1, the wavelengths of absorption peaks in solvent of

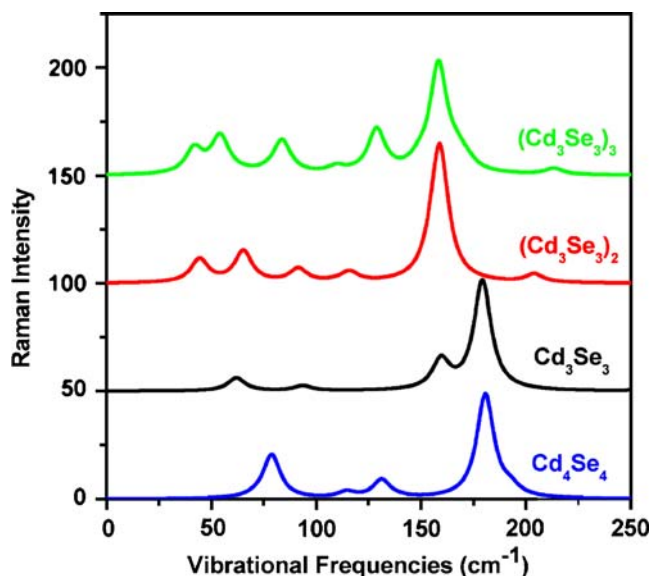


Fig. 3 Raman spectra for Cd_4Se_4 , Cd_3Se_3 , $(\text{Cd}_3\text{Se}_3)_2$ and $(\text{Cd}_3\text{Se}_3)_3$ molecules

Table 2 The lowest vibrational frequencies (cm^{-1}), absorption spectra (λ nm) and absorption spectra in water (λ W nm), bond lengths of Cd-Se and Cd-S (\AA) for Se-Cd-ligand molecules

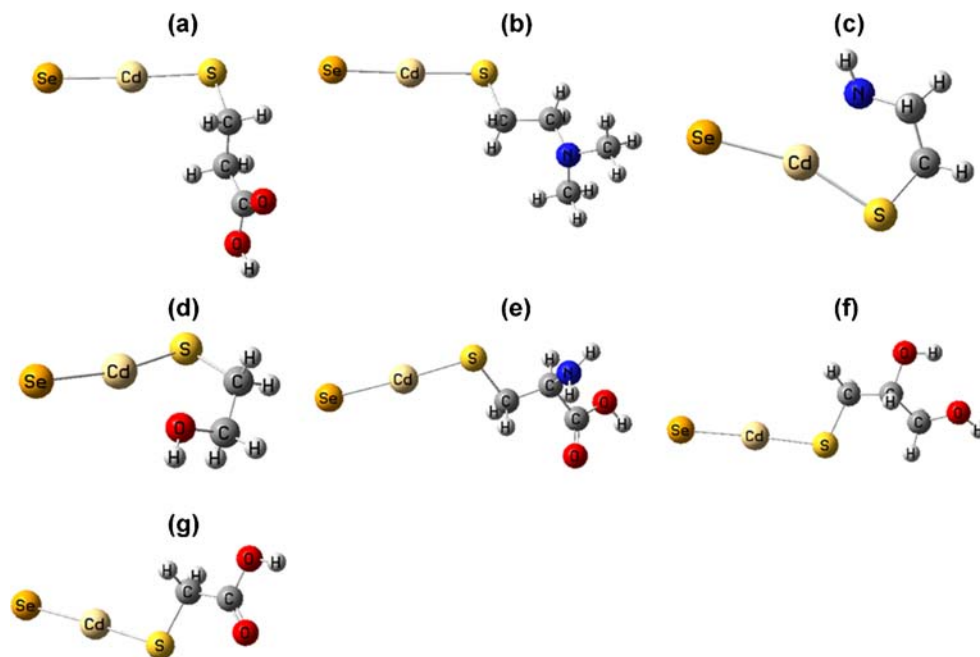
Se-Cd-ligand	Freq cm^{-1}	λ (nm)	λ (W)	B-L Cd-Se	B-L Cd-S
Se-Cd	231	4190	399	2.475	—
Se-Cd-S-CH ₂ -CH ₂ -COOH	16	456	292	2.584	2.469
Se-Cd-S-CH ₂ -CH ₂ -N(CH ₃) ₂	22	461	296	2.585	2.461
Se-Cd-S-CH ₂ -CH ₂ -NH ₂	44	380	281	2.619	2.508
Se-Cd-S-CH ₂ -CH ₂ (OH)	48	370	285	2.610	2.503
Se-Cd-S-CH ₂ -CH(NH ₂)-COOH	13	456	324	2.586	2.467
Se-Cd-S-CH ₂ -CH(OH)-CH ₂ (OH)	3.0	456	293	2.583	2.464
Se-Cd-S-CH ₂ -COOH	14	440	277	2.583	2.474

Cd_3Se_3 , Cd_4Se_4 , $(\text{Cd}_3\text{Se}_3)_2$ and $(\text{Cd}_3\text{Se}_3)_3$ structures are 336, 346, 365 and 387 nm which are shorter than those without water (507, 542, 499 and 530 nm). Furthermore, absorption spectra in solvent increase with the order of Cd_3Se_3 , Cd_4Se_4 , $(\text{Cd}_3\text{Se}_3)_2$ and $(\text{Cd}_3\text{Se}_3)_3$, while the results without solvent do not have this kind of rule. In experiment, it has been proved that the wavelengths of absorption spectrum shift to red when the size of nanocrystals increase, which is named as quantum size effect [20]. Obviously, absorption spectra in solvent are consistent with quantum size effect but data without solvent are paradoxical with this effect. Thus, we can speculate that solvents influence the qualities of CdSe nanocrystals. If there is no presence of solvent, some characters of nanocrystals cannot be represented, viz., solvent is an important term for the formation of nanocrystals. Moreover, all these absorption spectra in solvent of four clusters are smaller than those of experimental nanocrystals [21]. This is because these clusters are smaller than the sizes of experimental nanocrystals, which is also induced by the

quantum size effect. In a word, our data in solvent are perfectly consistent with the experiment rule. Besides, we also generated HOMO and LUMO figures of Cd_3Se_3 , Cd_4Se_4 , $(\text{Cd}_3\text{Se}_3)_2$ and $(\text{Cd}_3\text{Se}_3)_3$ structures (Fig. 2). From the analysis of orbital, we believe that Cd and Se atoms form valence orbital using $4d^{10}5s^2$ and $4s^24p^4$, respectively. The d orbitals of Se atoms do not participate in bonding. Moreover, there is d orbital in HOMO, but LUMO does not have d orbital. Thus, we deduce that the absorption peaks of Cd_3Se_3 , Cd_4Se_4 , $(\text{Cd}_3\text{Se}_3)_2$ and $(\text{Cd}_3\text{Se}_3)_3$ are the transitions from d to p orbitals, but not the d-d transition. Moreover, HOMO and LUMO figures show that Cd_4Se_4 molecule has strong delocalization, further indicating its good stability.

Raman spectra in the solvent were gained with $\text{Freq}=\text{Raman}$ (Fig. 3). As to II-VI nanomaterials, their Raman spectra are difficult to get in experiment. Thus, the calculation in theory of Raman spectra is significant, and the main problem in theory is the choosing of calculated method. In our paper, calculated Raman spectra of four structures are about 175 cm^{-1} , which is almost identical with

Fig. 4 The conformations of seven Se-Cd-ligand molecules



the experimental result that is proposed by Dzhaganin in 2008 [22]. Thus, comparable Raman spectra of CdSe are calculated in theory with our method that can also be used for other II-VI clusters. Calculated Raman spectra with DFT can offer guidance for future experimental investigation.

Influence of ligands in aqueous phase

In order to comprehensively investigate the mechanism of this kind of nanocrystals, we obtained a series of Se-Cd-ligand structures (Table 2 and Fig. 4). -S-CH₂-CH₂-COOH (a), -S-CH₂-CH₂-N(CH₃)₂ (b), -S-CH₂-CH₂-NH₂ (c), -S-CH₂-CH₂(OH) (d), -S-CH₂-CH(NH₂)-COOH (e), -S-CH₂-CH(OH)-CH₂(OH) (f) and -S-CH₂-COOH (g), that have thiol, which are common ligands for aqueous synthesis. Distinctly, bond lengths of Se-Cd in Se-Cd-ligand structures are longer than that of CdSe unit, viz. the ligands make the bond between Se and Cd weak. From this analysis, we can say that the bond among the CdSe nanocrystals is different from that in bulk CdSe materials. Moreover, except -S-CH₂-CH₂-NH₂ and -S-CH₂-CH₂(OH), other ligands have similar bond lengths and absorption peaks. -S-CH₂-CH₂-NH₂ and -S-CH₂-CH₂(OH) ligands have the same bond lengths and absorption spectra. Therefore, we speculate that -S-CH₂-CH₂-NH₂ and -S-CH₂-CH₂(OH) ligands should have the same influence to the CdSe nanocrystals in practical experiment and all ligands have similar influence for the synthesis of CdSe nanocrystals. We are looking forward to the investigation of experiment in this aspect. Besides, comparing the absorption spectra in solvent and in gas phase of Se-Cd-ligand clusters, we conclude that the solvent makes the absorption spectra shift to blue. Simultaneity, we can also prove that the ligand makes absorption spectra shift to blue too. Under these conditions (with solvent and ligands), calculated absorption spectra of four clusters beautifully correspond with those of CdSe nanocrystals, according to quantum size effect. Finally, through analysis of Raman spectra of Se-Cd-ligand, we detect that the whole Se-Cd-S does not vibrate and ligand makes CdSe nanocrystals stable, which is one function of ligand.

Conclusions

In summary, we obtained four structures and many Se-Cd-ligand clusters with DFT/ B3LYP/Lan12dz method. Cd₃Se₃ and Cd₄Se₄ have similar characters as wurtzite and zinc blende for (Cd₃Se₃)₂ and (Cd₃Se₃)₃ molecules (the simplest structures composed of hexagons) have comparable qualities with Cd₃Se₃ structure, according to quantum size effect. First, through study of Cd₃Se₃, Cd₄Se₄, (Cd₃Se₃)₂ and (Cd₃Se₃)₃ molecules, we find that Raman peaks of CdSe is about 175 cm⁻¹ which is almost consistent with the

experiment results. Second, employing TDDFT to calculate the absorption spectra, we detect that both solvent and ligands make absorption spectra shift to blue. Under these conditions, the calculated absorption spectra are identical with experimental results according to quantum size effect which has been a universal phenomenon in CdSe nanocrystals. Besides, HOMO-LUMO figures show that all transitions of these absorption peaks are from d to p orbitals. Moreover, HOMO-LUMO gaps become smaller with the order of Cd₃Se₃, (Cd₃Se₃)₂ and (Cd₃Se₃)₃. Therefore, we can control the number of atoms to increase the band gap. Finally, analytical results of Se-Cd-ligand testify that all ligands have a similar influence on CdSe nanocrystals. In conclusion, investigated characters in this paper are important and significant for experiment.

Acknowledgments This work was supported by the National Natural Science Foundation of China under Grant NO.60877024.

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