Chiroptical activity in colloidal quantum dots coated with achiral ligands

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Abstract: We studied the chiroptical properties of colloidal solution of CdSe and CdSe/ZnS quantum dots (QDs) with a cubic lattice structure which were initially prepared without use of any chiral molecules and coated with achiral ligands. We demonstrate circular dichroism (CD) activity around first and second excitonic transition of these CdSe based nanocrystals. We consider that this chiroptical activity is caused by imbalance in racemic mixtures of QDs between the left and right handed nanoparticles, which appears as a result of the formation of various defects or incorporation of impurities into crystallographic structure during their synthesis. We demonstrate that optical activity of colloidal solution of CdSe QDs with achiral ligands weakly depends on the QDs size and number of ZnS monolayers, but does not depend on the nature of achiral ligands or polarity of the solution.

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1. Introduction

Chirality is a property of the object whose chemical, crystallographic and certain optical characteristics differ from its mirror image. It is one of the important factors in molecular recognition, which has many practical uses in chemistry and biology [1]. Chiral compounds are the basic "building blocks" of the living world. Moreover, the living systems biomolecules such as DNA, RNA, carbohydrates, proteins and fragments of these structures are homochiral (i.e. they are enantiomers). It is known, that different enantiomers can have various taste and flavor, have different toxicity or opposite therapeutic effects. It is not surprising that in pharmaceutical production value of chiral drugs considerably increased.

However, until now the origin of substances with different chirality in the nature remains open. The investigation of the origin of chirality in nanostructures such as metallic nanoparticles or quantum dots (which also called artificial atoms) might allow better understands this issue.

To date the chirality of semiconductor and metallic nanoparticles and nanostructures has been studied by number of research groups [2–10]. It was demonstrated that particularly

chiral nanoparticles are very promising for biosensing application, chiral memory, nanoassemblies and nanofabrication of the chiroptical devices [2–10].

Chiroptical activity in CdS semiconductor QDs stabilized with chiral molecules D- and L-pennicillamine has been first demonstrated by Gun'ko and associates [7, 8]. The effect of optical activity of CdS QDs has been explained by pennicillamine-induced distortion of crystallographic order of surface Cd atoms which extends an enantiomeric structure to the nearsurface layers and causes the modification of associated electronic states of QDs in this region, while the core of nanoparticles is found to remain undistorted and achiral (amphichiral). Similar chiroptical activity of QDs stabilized with natiomers has been observed for CdTe QDs [9]. It was suggested that the atomic origin of chiral sites in QDs is topologically similar to that in the organic compounds. Since atoms in CdTe QDs are arranged as tetrahedrons, chirality can occur when all tetrahedral apexes have different chemical substitutions. Later it was reported that CD activity in CdTe QDs can be preserved even after the replacement of the chiral surfactant molecule by an achiral one [10].

In more recent works the size and material dependence of the chiroptical activity of semiconductor QDs were systematically examined [11–13] The analysis of the chiroptical induction caused by these factors leads to the conclusion that it is primarily an electronic interaction effect between the adsorbed chiral molecules and the electron-hole states of QDs [11]. Proposed mechanism of the induced chirality is shown to be consistent with the hybridization and coupling of the molecular orbital of chiral ligand with the QD valence band states [13].

In their recent work Gun'ko and associates [14] reported the evidence of the intrinsic chirality of CdSe/ZnS QDs with wurtzite crystal lattice stabilized by achiral ligands. Similar to the CdTe QDs [6], ensembles of CdSe/ZnS nanoparticles have been found to be a racemic mixture of left- and right- handed nanoparticles which also contains a fraction of nonchiral QDs. It was suggested that the intrinsic chirality of QDs might be caused by the presence of naturally formed chiral defects [14]. The results of this study hint on the intrinsic chirality of core-shell CdSe/ZnS QDs which presumably is caused by some chiral defects forming at the surface of QDs or at interface between core and shell. Indeed, crystallographic disorder in near-surface region of colloidal nanoparticles is inevitable, arising, in the case of CdSe/ZnS QDs, from the modification of the crystallographic structure of the ZnS shell and the reconstruction of the CdSe/ZnS interface [15]. Although the formation of defects associated with atomic displacement at the interface during growth core-shell QDs cannot be eliminated, it can be minimized, for example using core and shell materials of the same crystallographic structure. Therefore, to understand the intrinsic chirality of core-shell QDs in more detail we investigated the core CdSe and core-shell CdSe/ZnS QDs with a cubic lattice structure.

In all previous studies discussed, the chiroptical activity of QDs have been induced by the initial presence of chiral ligand molecules [11–13], by the enantioselective phase transfer using an appropriate chiral ligand [14] or by the illumination of dispersions of racemic nanoparticles with circularly polarized light [6]. Here we report the observation of CD activity in the spectral region of excitonic absorption peaks for CdSe and CdSe/ZnS QDs with the cubic lattice structure which were initially prepared without use of any chiral molecules and coated with achiral ligands.

2. Methods and characterization techniques

CdSe core-shell colloidal QDs were synthesized according to the procedures published by Chen et al. [16] without using any chiral chemicals. Initially hydrophobic QDs were solubilized in water with DL-cysteine using protocol developed by Sukhanova et al. [17]. CdSe QDs with a different number of ZnS layers were purchased from PlasmaChem GmbH (Germany).

Doubly purified deionized water from an 18 MU Millipore system was used for all dilutions. UV-Vis Cary 50 (Varian) and Cary Eclipse fluorescence spectrophotometer were

used to measure the absorption and photoluminescence (PL) spectra in solution, respectively at 20 °C. CD spectra were recorded at 5 °C using Jasco J-815 CD spectrometer. A quartz cuvette with a 2 mm path length was used for all CD experiments. The crystallographic structure of the samples was examined using X-ray powder diffraction (XRD) on PANalytical's X'Pert PRO MRD system.

All QDs studied in this work have cubic lattice structure, which was confirm by XRD measurement (Fig. 1).
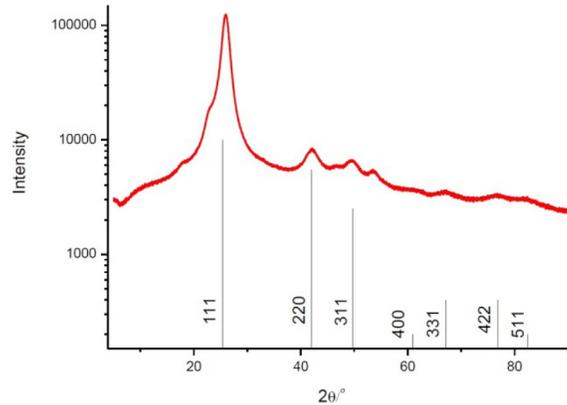

Fig. 1. X-ray Diffraction spectra of CdSe QDs. The stick pattern shows the positions of standard XRD peaks for bulk zinc blende CdSe with cubic lattice structure [18].

3. Results and discussion

First we have studied the optical properties of CdSe QDs with different sizes ranging from 2.7 to 4.5 nm. The absorption and PL spectra of these semiconductor QDs in toluene solutions are shown in Fig. 2.
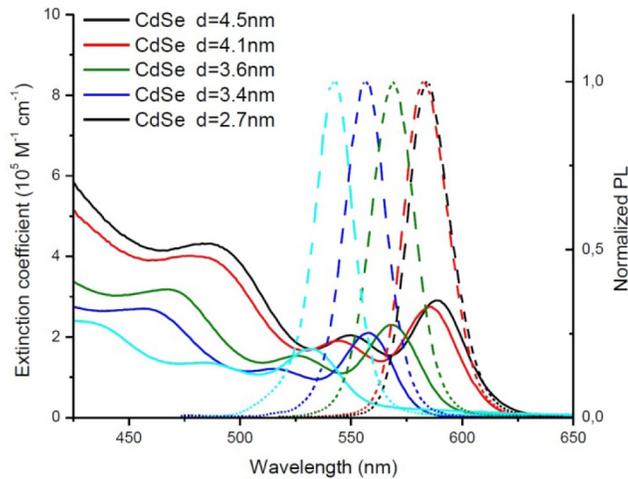

Fig. 2. Absorption (solid lines) and PL (dashed lines) spectra of toluene colloidal solutions of CdSe QDs of different sizes ranging from 2.7 to 4.5 nm solubilized with TOPO. (The PL excitation wavelength λ_{exc} = 450 nm).

It is well known that the size of QDs determines the value of the extinction coefficient and position of the absorption and fluorescence spectral bands of these nanoparticles.This property, from the other hand, gives the possibility to estimate the molar absorption

coefficient and the size of QDs from experimentally detected position of the first excitonic transition [19].

The CD spectra of CdSe QDs of different sizes (initially prepared without any chiral molecules and coated with achiral trioctylphosphine oxide (TOPO) ligand) displays a weak optical activity around first and second excitonic transition with positive Cotton effect which is typical for left-handed helix structures (Fig. 3).
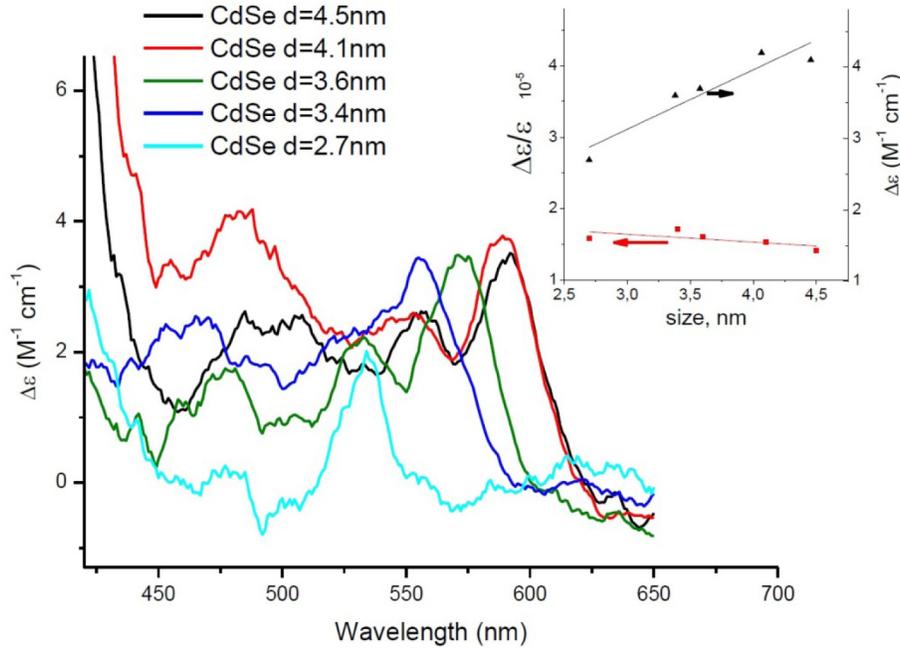

Fig. 3. CD spectra of toluene colloidal solutions of CdSe QDs of different sizes ranging from 2.7 to 4.5 nm. Inset represents the size dependence of molar CD extinction coefficient (black triangle) and g-factor of dissymmetry (red foursquare) of CdSe QDs.

The value of molar circular dichroism grows with an increasing of QDs size proportionally to the molar extinction coefficient of CdSe QDs. At the same time anisotropy g-factor or dissymmetry factor ($g = \Delta\varepsilon/\varepsilon$) of these CdSe QDs slightly decreases with an increasing of the size of the QDs (Fig. 3, inset).

It is noteworthy that dependence of CD activity and dissymmetry factor on the size of QDs still remains controversial, although this correlation has been studied by number of research groups using CdSe nanoparticles coated with chiral ligands. It was shown that an increase of QDs size leads to a decrease in optical activity of nanoparticles [11]. Also the dissymmetry g-factor was found to decrease almost exponentially with an increasing of QDs size. It should be noted that in Ref [11]. only CdSe QDs of small size (less than 2 nm) were investigated. The same phenomenon i.e. decreasing of an optical activity with an increasing of the size of QDs was reported for larger CdSe nanoparticles [12]. Controversionaly, in later work [13] no obvious correlation between size and g values was found for CdSe QDs (2 ÷ 5 nm in size) solubilized by chiral D and L cysteine [13].

It comes as no surprise that observed optical activity of QDs with achiral ligands is much weaker as compared to nanoparticles coated with chiral molecules. This is probably why much less attention was paid by researchers to the QDs coated with amphichiral ligands. However the values of dissymmetry factor g for CdSe QDs with amphichiral ligands only 5-10 times smaller than these observed for similar sizes CdSe QDs coated enantiomers [11–13].

Thus the own chirality of the colloidal solution of CdSe QDs with achiral ligands is caused by the presence in a solution of unequal ratio of left and right handed intrinsic chiral nanoparticles. Based on positive optical activity we can conclude that there is a slight predominance of left- over right- handed chiral nanoparticle in CdSe QDs solution.

It was demonstrated that for CdTe QDs the replacement of chiral ligands by an achiral one practically does not change the CD activity [10] however in light of discovered effect of own chirality of the colloidal solution of CdSe QDs (Fig. 3) it will be instructive to know to what extend CD properties of these QDs can be affected by replacement of achiral ligands and type of solvent. To investigate this effect hydrophobic CdSe QDs coated with TOPO and dissolved in toluene were solubilized with DL-cysteine and redissolved in aqueous solution. The absorption, PL and CD spectra of CdSe QDs in water and toluene are presented in Fig. 4. One can clearly see the changes in the absorption and PL spectra of CdSe QDs after solubilization with cysteine and redissolving. The main features observed after solubilization are blue shift of the absorption peak (centered around 580 nm prior solubilization) and the decrease of optical density in the spectral region of the second absorption peak (indicated by arrow in Fig. 4). Also after solubilization of QDs with DL-cysteine we found the decrease of fluorescence quantum yield and an increase in the width-at-half-maximum of the PL band. However all these substantial changes in the absorption and PL spectra, which associated mainly with the modification of surface layer of QDs and the difference in the polarity of the solution, do not strongly affect lineshape of the CD spectrum. Following solubilization the CD spectrum of CdSe QDs in water also shows slight blue shift in the region of first maximum and some small changes in the lineshape as compared to spectrum of CdSe QDs in toluene. However in general, CD spectra of CdSe QDs coated with DL-cysteine and coated with TOPO are quite similar and have the same value of dissymmetry factor g despite the difference in polarity of the solution (polar water and nonpolar toluene, respectively).
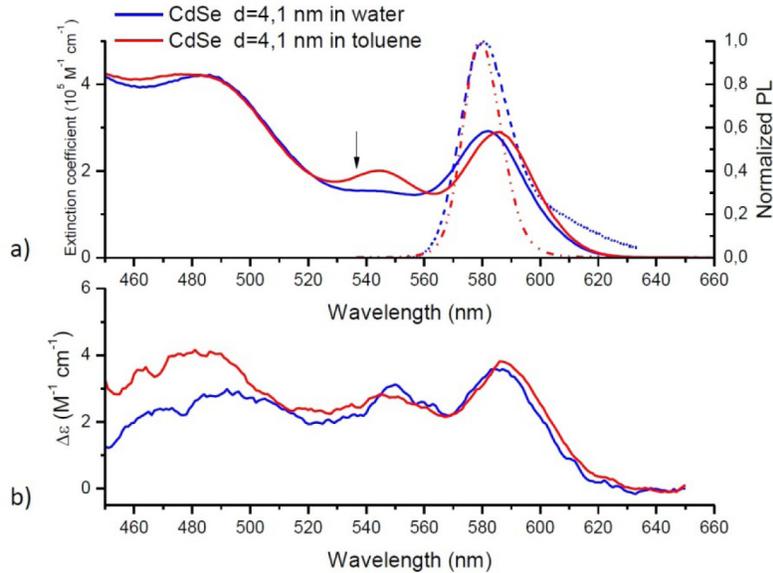

Fig. 4. a) Absorption (solid lines) and PL (dashed lines) spectra of CdSe QDs 4.1 nm size in water solution coated with DL-cysteine (blue) and in toluene coated with TOPO (red). PL excitation wavelength λ_{exc} = 450 nm. b) CD spectra of CdSe QDs 4.1 nm size in water solution coated with DL-cysteine (blue) and in toluene coated with TOPO (red).

Therefore the replacement of achiral ligands and dissolution in other solvents which lead to significant changes in the absorption and PL spectra practically do not affect the CD

spectra of QDs. Thus we have to conclude that replacement of achiral ligands does not lead to significant changes in the quantum dots surface chirality and obviously does not affect the core of nanocrystals.

It is well know that deposition of surface semiconductor layer with bandgap bigger than that of the core material results in strong enhancement of oscillator strength and PL efficiency of QDs [20]. It is intriguing to investigate whether or not a deposition of such a layer might result in modification of CD activity of QDs. The first attempt to address this question was made recently using CdSe QDs with hexagonal crystallographic structure passivated by shell of cubic ZnS with fixed thickness [14]. As were mention above the formation of defects associated with atomic displacement at the interface during growth core-shell QDS can be minimized by using core and shell materials of the same crystallographic structure. In this way the effect of the interface defects on chiroptical activity of QDs can be much weaker, opening the possibility to investigate CD properties of core-shell nanoparticles in more detail. This was the main idea behind our next experiments in which CD activity of CdSe/ZnS QDs with cubic crystallographic structure of both core and shell was studied. Also because the reconstruction of the CdSe/ZnS interface strongly depends on thickness of the shell [15], we investigated CD properties of the set of samples coated with an increasing numbers of ZnS layers.

The absorption, PL and CD spectra of uncoated CdSe and CdSe/ZnS QDs (with number of ZnS layers ranging from 1 to 5) which were solubilized with TOPO are shown in Fig. 5. The molar extinction coefficient was found to be almost identical for all these samples.
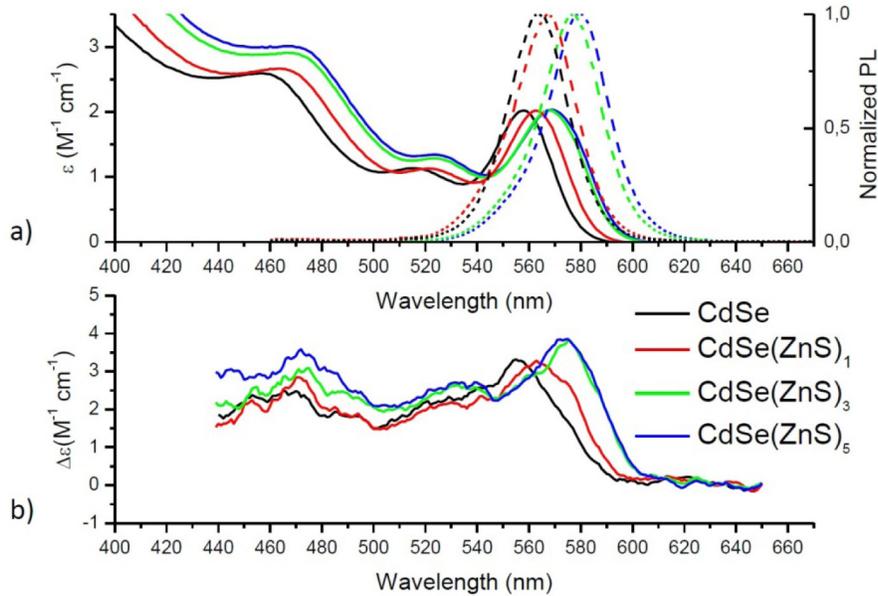

Fig. 5. a) Absorption (solid lines) and PL (dashed lines) spectra of CdSe and CdSe(ZnS) QDs (with different number of ZnS layers ranging from 1 to 5) in toluene b) CD spectra of CdSe and CdSe(ZnS)$_n$, n = 1-5 QDs 3.4 nm size in toluene.

Despite the fact that the lineshape of CD spectrum does not change much for samples containing CdSe QDs with increasing number of ZnS monolayers, we observed a small but clearly detectable increase in an optical activity and g-factor (Fig. 5 and 6). It is noteworthy that increased shell thickness (i.e. number of ZnS layers) means an increase in the amount of deposited material as well as slight increase of the QDs size. Previously it was shown that for QDs coated by chiral ligands optical activity strongly depends on the chemical composition

of QDs [11–13]. At the same time the deposition of ZnS layers does not significantly modified the shapeline and intensity of CD spectra of CdSe QDs. Thus the formation of the defects associated with atomic displacement at the interface during growth of core-shell QDs with the same crystallographic structure is not the main factor responsible for the intrinsic chirality of CdSe/ZnS QDs.
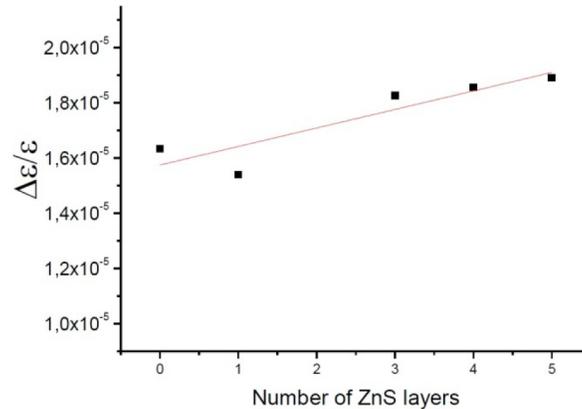

Fig. 6. Dependence of dissymmetry g-factor on the number of ZnS monolayers for CdSe QDs.

It is also important to note that for different CdSe QDs we observed domination of left handed particles or small clusters in solution (Fig. 3 and 5). This is probably caused by the fact that for synthesis of both CdSe colloidal QDs, which were prepared in our group, and CdSe/ZnS QDs, which were purchased from PlasmaChem, were used the same chemicals and synthesis procedure. Therefore we believe that the chemical composition and the specific characteristics of the synthesis determine the predominance of the left or right chiral nanocrystals in solution.

The origin of chirality of QDs with centrosymmeric cubic structure is not clear at the moment and requires further investigation. A large number of factors can influence the formation of chiral nanoparticles or clusters even when achiral ligands have been used.

It is known that some molecules becomes chiral upon an adsorption on metal surface due to the symmetry-breaking interactions with the surface atoms, even if the metal surface is not chiral [21–23]. Also it was reported [24–27] that achiral molecules can form chiral patterns on achiral surfaces by the distortion of crystallographic order of atoms. Such phenomena have been studied on metal surfaces and metal clusters or nanopasrticles protected by achiral ligands [21–27]. Moreover it was recently shown that in case of CdTe and CdSe QDs coated with achiral ligands both individual semiconductor nanocrystals and their clusters can be chiral [6, 14], but their colloidal solutions of semiconductor nanoparticles are racemic and contains equal amount of different enantiomers. However it is turned out that the preferential formation of right- (or left-) handed nanostructures made of cubic CdTe nanoparticles can be induced by the illumination of the dispersions of racemic CdTe NPs with right- (left-) handed circularly polarized light [6]. This effect is based on the enantio-selective photoactivation of chiral NPs and clusters, followed by their photooxidation and self-assembly into nanoribbons with specific helicity driven by chirality-sensitive interactions between NPs with tetrahedral cores.

Potentially, any QDs can be chiral since they frequently have the reduction in symmetry due to the presence of chiral defects in bulk and at the surface [14]. Another scenario is that the adsorption of low symmetry achiral ligands on the surface of QDs leads to the induction of the chirality of individual QDs. There are several mechanism to be taken into consideration: a) the surface electronic structure of QDs covered with low symmetry achiral

ligands can become chiral b) achiral ligand and QD response become chiral due to Coulomb interactions or due the electron hybridization [28].

Under an ideal conditions, the formation of chiral nanoparticles or small clusters should lead to equal amount of left and right handed nanostructures. However, it should be noted that in reality, synthesis of QDs might be accompanied by the formation (although with small probability) of various defects or an incorporation of an impurities into crystallographic structure. For example the formation of screw dislocations can occur during the hot injection synthesis of CdSe/ZnS quantum dots and rods [14]. Also during the synthesis the nanocrystals are exposed to stirring, vortex and also can be affected by illumination by circularly polarized light. It is noteworthy that only 2% of chiral molecules is sufficient to prevent the formation of one of the enantiomorphous lattices on the metallic surface [23]. Thus even a slight deviation from the symmetry in small amount of QDs or clusters during the synthesis or even the presence of small amount of chiral impurities can create an imbalance between the left and right handed nanostructures, and leads to a small optical activity of QDs solution. Indeed, a small value of the optical activity of QDs observed in present work could be explained by above described mechanisms of breaking of the global chiral symmetry in a solution. It is a very interesting question directly related to the appearance of chirality of life. Our studies have shown an amazing sensitivity of the colloidal QD system to the breaking chiral symmetry due to small factors in our experiments. It seems that complex systems can be always chiral macroscopically at least to some extend. At the nanoscopic scale, every QD can be chiral because of the defects. Our experimental data presented in Fig. 3-5 illustrates the above ideas.

4. Conclusions

We demonstrated that CdSe and CdSe/ZnS QDs with a cubic lattice structure which were initially prepared without use of any chiral molecules and coated with achiral ligands originally have small CD activity in the spectral region of first and second excitonic transition, which slightly depends on the QDs size and number of ZnS monolayers, but does not depend on the nature of achiral ligands or polarity of the solution. We consider that the intrinsic chirality of colloidal CdSe and CdSe/ZnS QDs with amphichiral ligands is caused by the formation of various defects or incorporation of an impurities into crystallographic structure during their synthesis. These defects can create imbalance in racemic mixtures of QDs between the left and right handed nanostructures, and leads to a small optical activity of CdSe based nanocrystals.We believe that our work marks an important step toward better understanding of intrinsic chirality of colloidal CdSe QDs, which might have potential application in biosensing, toxicology, drug delivery system, chiral information transfer and other uses. Discovering the specific factors which determine imbalance between the left and right handed nanostructures in colloidal solutions of QDs would allow us to come closer to the understanding the origin of chirality in nature.

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