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Research on Ligand Properties of CdSe Quantum Dots

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Abstract. The surface ligands not only provide quantum dots nanocrystals (QDs) colloidal stability and workability of QDs particles, but also play an important role in passivation of QDs surface defects and change of electron transport characteristics of QDs films. The quantum dots synthesized with different ligands differ greatly, and the properties of QDs synthesized using the same ligands under different reaction conditions are also different. Previous studies have shown that surface ligands can greatly improve the stability of quantum dots, but ignore the effect of surface ligands on the luminescent properties of quantum dots. The electrochemical properties of ligands around quantum dots have a great influence on their luminescent properties. In this paper, the application of ligands in QDs is briefly described, and the effect of ligands on the photoluminescence of CdSe was investigated experimentally.

1. Introduction

In recent years, the optical properties of semiconductor nanocrystalline (NCS) have been studied actively. Semiconductor quantum dots (QDs) is a kind of particles with nanoscale diameters. Due to their excellent properties including pure emission colours, adjustable bandgaps and high luminance efficiency, they are of great interest in many fields such as light emitting diodes (LEDs), solar cells, bio-imaging and ECT. [1]. The optical and electronica properties of QDs can be tailored by controlling their size, shape and composition. Besides, surface defects such as hanging-bonds resulted from the large surface area-to-volume ratio will quench the quantum yields (QYs) and the luminous intensity of the dots. The effect of ligands on the luminescent properties of quantum dots is determined by their electrochemical properties. Specifically, ligands can increase or decrease the fluorescence intensity of QDs. For example, for the well-known CdSe NCs, prepared by standard methods in trioctylphosphine oxide (TOPO), the replacement of TOPO ligands by amines increases the fluorescence intensity, whilst that by thiols leads to a complete fluorescence quenching. Therefore, surface ligands play an important role in functionalize the properties of QDs. In this paper, the effects of several CdSe NCs surface-contact ligands on the optical properties of NCs have been systematically studied. The CdSe quantum dots with different ligands have been chemically synthesized, and their optical properties have been measured and analyzed.

2. The Entropic Ligand and Classification of Ligands

It has been verified that ligands modify the QD surface, neutralize the surface hanging-bonds, assist them exhibiting diverse properties, and provide them with stability and improved performance in devices. [2] The ligand exchange reaction has greatly expanded the variety and functional diversity of QDs materials. Organic, inorganic ions, clusters and polymers can all be used as QDs ligands. Ligands are labelled as L-, X- or Z-type respectively; according to the number of electrons (2, 1 or 0) they donate to the QD-ligand band. [3]. Neutral double electron donors, such as amines (RNH_2), phosphine (R_3P) and phosphine oxide (R_3PO), have an isolated pair of electrons that directly coordinate the

surface metal atoms, which can be called L-type ligands. The X-type ligand is neutral and has odd valence-shell electrons, requiring a single electron from the surface site of the QDs to form a double electron covalent bond. Common X-type ligands such as carboxylate ($RCOO^-$), thiolates (RS^-) and phosphonates ($RPO(OH)O^-$), and inorganic ions (Cl^-, $InCl_4^-$, AsS_3^{3-}) or bound ion pairs ($Net_4^+I^-$) dissolved in non-polar solvents. Z-type ligands (such as Pb $(OOCR)_2$ or $CdCl_2$) can bind to the surface of QDs in the form of a double electron receptor at the electron-rich Lewis basic site. [3].

Recent studies have shown that the external quantum efficiency of the light-emitting diode devices fabricated with QDs has achieved more than 20% results. [4, 5]. QDs, their surface ligands and device structures all have influence on the luminous performance of the QLEDs. By using Dodecane-thiol capped CdSe/CdS QDs as active materials, device of the multilayer structure of ITO/PEDOT: PSS/poly-TPD/PVK/QDs/PMMA/ZnO/Ag, exhibits red emission peaked at 640 nm and reaches a very high external quantum efficiency of 20.5%. [1]. However, when decylamine and OA are used as ligands, the EQE of QLED fabricated by using CdSe/CdS quantum dots as luminescent layer and Ito/ZnO/QDs/NPB/LG101/AL as device structure is also up to 18.5%. [1].

Therefore, the selection of ligands plays an important role in the further application of QDs. The results show that the QDs with small ligands will facilitate the charge transport of the light-emitting devices and drive the QLEDs effectively. [6]. However, the distance between QDs is the main factor to determine the stability of QDs solution, and the solubility of QDs is reduced with the smaller size of ligand. [7]. In recent experiment of Xiaogang Peng, the concept of entropic ligands [8]. was proposed and the solubility of QDs was quantitatively expressed by the following equation:

$$\chi = e^{\frac{-\Delta^m H_{NC}}{RT}} e^{\frac{\Delta^m S_{NC}}{R}} \quad (1)$$

Where the $\Delta^m H_{NC}$ is partial molar mixing entropy of the QDs dissolving in a liquid and the $\Delta^m S_{NC}$ is molar conformational entropy, which accounts for melting entropy of the QD solid. The solubility of CdSe nanocrystals in organic solvents is greatly improved by the use of entropy ligands. According to the basic principle of entropy ligands, CdSe/CdS core/shell QDs synthesized from dodecanoic acid/oleic acid and tetradecanoic acid/oleic acid has excellent optical properties. At the same time, the solubility and charge transport performance of CdSe/CdS QDs have also been greatly improved, so it is hopeful to produce more efficient QLED.

CdSe quantum dots are widely used in light emitting diodes (LEDs), biomarkers and solar cells because of their good size fluorescence spectra and the change of ligands on the surface of QDs will affect the fluorescence effect of QDs. Electronic structure and photoelectric conversion efficiency in optoelectronic devices. Therefore, we discuss the effects of different ligands on quantum dots in an experimental manner.

3. Effects of Ligands on CdSe Quantum Dots

3.1. Chemicals

Trioctylphosphine (TOP, 90%), cadmium acetate hydrate (99.99%), cadmium oxide (CdO, 99.99%), triocctylphosphine oxide (TOPO, 98%) were purchased from Macklin. Selenium powder was purchased from Hushi of Shanghai. Oleic acid (OA, 90%) and octadecylphosphonic acid (ODPA, 98%) are purchased at Aldrich and Beijing HWRK CHEM, respectively.

3.2. Experimental Procedure

3.2.1. TOPO capped CdSe QDs were synthesized by solution method. [9]. At room temperature, 3 g TOPO and 0.025 g cadmium acetate were mixed into three-neck round-bottom of 25 ml specification, and then heated to 130 °C under the condition of full nitrogen. The process was accompanied by intense stirring. The reactor vacuumed at 130 °C for 40 minutes, and then increased to 330 °C under nitrogen condition. When the temperature of the reactor reached 330 °C, the Se precursor was injected into the three-neck round-bottom quickly through a syringe, and the reaction was cooled quickly. The Se precursor is prepared from 0.04 g Se powder dissolved into 1 g TOP.

3.2.2. ODPA capped CdSe QDs were synthesized by using of a reported solution method. [10,11]. 0.06 g of cadmium oxide, 3 g of TOPO and 0.28 g of ODPA were packed into the three-neck round-bottom of 25 ml. Then 0.058 g selenium powder was completely dissolved in 0.36 g TOPO to prepare Se precursor (TOPSe). The solution in the three-neck round-bottom is heated to 130 °C under nitrogen condition, and vacuum is pumped at 130 °C for 30 minutes, then the nitrogen is filled in and gradually heated to 330 °C, the colour of the solution becomes transparent during the heating process. When the solution is heated to 330 °C, the 1.8 ml TOP is injected rapidly, and the Se precursor is injected quickly after the temperature recovers and the reaction is cooled quickly.

3.2.3. OA capped CdSe QDs were synthesized by solution method. Similar to the synthetic ODPA-CdSe QDs, 1 ml oleic acid and 8ml octadecene were injected into the three-neck round-bottom, and then were stirred strongly by adding 0.3 mmol CdO, and the gas in the device was extracted at 130 °C by heating up to 130 °C under the condition of nitrogen. 0.236 g of Se powder was dissolved into 0.5 ml TOP to prepare Se precursor. When the temperature is raised to 330 °C, the Se solution is injected quickly and removes the temperature of the reactor.

3.3 Results and Discussion

CdSe QDs with TOP, ODPA and OA as ligands were synthesized respectively. There into, by controlling the reaction temperature and reaction time, ODPA-capped CdSe QDs were also prepared. Figure 1 (a) shows the digital photographs of these QDs dispersed in hexane. Their corresponding absorption and photoluminescence spectrum are shown in figure 1 (b) and 1 (c)

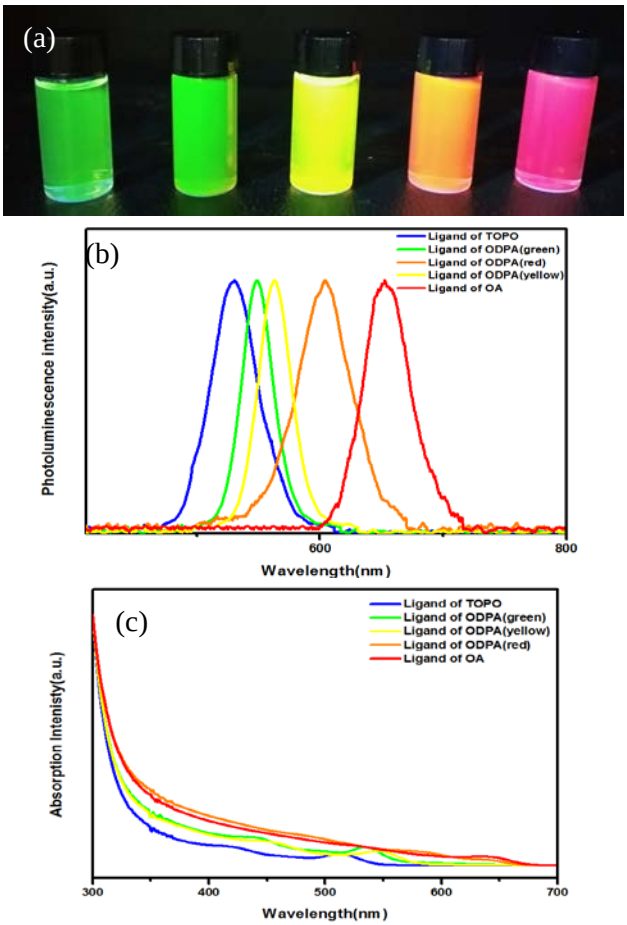

Figure.1 (a) From left to right are CdSe QDs with no ligand, with ODPA as ligand (emission peaks of 547 nm, 562 nm, 605nm respectively) and the CdSe with OA ligand.
(b) The absorption and (c) PL spectra of the QDs, respectively.

It can be seen from figure (1) that, CdSe QDs with different ligands exhibit different emission wavelengths. One of the main reasons for this is the size effect of QDs, and another reason for this can be attributed to the increase of HOMO edge of ligand. [12]. Table 1 lists highest-occupied and lowest-unoccupied molecular orbitals (HOMOs and LUMOs) of the organic ligands that common bind to the QDs surface.

Table 1. The HOMO and LUMO [eV] of Common surface ligands

Surface ligand	HOMO	LUMO
1:Trioctylphosphine oxide	-5.722	-0.281
2: Oleic acid	-6.572	-0.179
3: Octadecylphosphonic acid	-6.376	0.131

Furthermore, for ODPA-capped CdSe QDs, their peak wavelengths can be adjusted by controlling the reaction temperature and reaction time.This phenomenon can be attributed to the size effect of QDs. Because the internal electrons and holes in the QDs are limited by the size of the space, the energy will be quantized, the continuous band will be changed into a discrete energy level structure, and the band gap will be widened, resulting in the changes of the absorption and fluorescence spectra of the QDs. In the study of QDs, it is found that with the increase of the size of QDs, the photoluminescence peak value will be redshift. The size of QDs is estimated by transmission electron microscopy (TEM) measurements.

4. Conclusion

In this paper, we review the classification of quantum dot ligands in recent years, and describe the concept of entropy ligands. The effects of several ligands on the properties of CdSe colloid quantum dots were studied experimentally. We observed that the absorption and fluorescence of QDs changed greatly when we exchanged different ligands, which has a great relationship with the electron energy levels after binding between QDs and ligands by theoretical analysis. Basically, the photoluminescence of, CdSe NCs is increased by the use of the ligand HDA, TOP, pyridine and some acetate, and decreases with the use of thiols. Therefore, due to the excellent effect of QDs in many fields and the remarkable modification of QDs by surface ligands, the surface science of QDs is particularly important.

5. References

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