Study on the Photoluminescence Properties and First-Principles Calculations of L-cysteine Capped ZnS Quantum Dots

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Abstract. L-cysteine (L-cys) was used to coat ZnS quantum dots (QDs), which should benefit the improvement of water solubility and photoluminescence (PL) intensity of ZnS QDs. The impact of L-cys on the performances of ZnS QDs and the corresponding mechanism were discussed. It illustrated that L-cys modification didn’t change the crystal structure of ZnS QDs, and the mean diameter was enlarged as the content of L-cys was more. The results also displayed that the water solubility and PL intensity of samples coated with L-cys was better than that of the uncoated sample. The sample exhibited the maximal emission while the weight ratio of L-cys to QDs equaled 1.4:0.5, and it was 4.5 times as strong as ZnS sample. The result of the First-principles calculations indicated that L-cys shell layer is beneficial to prolong the lifetime of photon-generated carriers at surface location, which should lead to a reduction in the nonradiative recombination on the surface, and then the PL intensity will be enhanced. This work helps to investigate the surface modification of QDs modified by other organic compounds.

Keywords: quantum dots, ZnS, L-cysteine, first-principles, photoluminescence

1. Introduction

As a semiconductor quantum dots (QDs), ZnS QDs have been attracting more and more consideration due to their excellent photoluminescence (PL) properties, and have shown great application potential in many fields such as bio-phosphorescent detection, medical imaging, nano-probes and biosensors [1-4]. However, ZnS QDs are inorganic compounds synthesized by chemical methods, which are not only poorly water soluble but also exhibit low fluorescence quantum yield. These factors hinder their application in the biomedical and photoelectrical field [5,6]. Many teams have carried out work to solve the questions mentioned above, such as by cations doping (for example rare earths and transition metals) [7-10], anions doping (halogen and oxygen) [11-13] and coating with inorganic materials [14-
An increase in PL intensity was all observed in these studies but their water-solubility didn’t be improved.

Surface modification with a non-toxic, hydrophilic and wide-band gap organic material is a valid way to enhance the PL and water solubility of ZnS QDs at the same time. L-cysteine (L-cys) [19], Pluronic 68 (F-68) [20], polyethylene glycol (PEG) [21] and mercaptoacetic acid [22] are commonly used to modifying the surface of QDs. Among them, as a common amino acid in vivo, L-cys is non-toxic and easily soluble in water. The QDs modified by L-cys exhibited strong luminescence, good water-solubility and biocompatibility. For example, Bian et al [1] synthesized water-soluble L-cys coated ZnS:Mn QDs with strong phosphorescence emission by hydrothermal method. Gong et al [19] fabricated water soluble CdTe capped by L-cys QDs by one-pot method, and the fluorescence of L-cys/CdTe QDs was increased by 1.3 times. Wang et al [23] prepared L-cys-coated Cy-CdS QDs with strong fluorescence and good water-solubility by liquid phase method. Copur et al [24] synthesized L-cys modified carbon QDs using a two-step method, and the results showed that L-cys significantly improved the PL intensity of carbon QDs. Duran et al [25] obtained L-cys modified CdSe/ZnS core/shell structure QDs with a strong yellow-green emission, with a good and renewable light stability and acceptable quantum yields via microwave irradiation by substituting hydrophilic heterobifunctional thiol ligands L-cys for the initial hydrophobic ligands of CdSe/ZnS QDs. However, the mechanism research on the influence of L-cys on the PL performance and electronic structure of QDs are rarely reported.

The first-principles calculations, which are based on the Density Functional Theory (DFT) framework, have been widely used to study the energy band structure, lattice dynamics and optical properties of doped semiconductor materials, which can provide theoretical references for experimental researches [26-30]. However, the report on the first-principles calculations of ZnS QDs capped by L-cys isn’t found up to now.

Here, ZnS QDs with L-cys cladding were prepared by two-step method, and the impacts of L-cys on the diameter, crystalline structure, water solubility, surface morphology and PL of ZnS QDs were researched. The energy band structure of L-cys modified ZnS QDs were investigated via DFT method, which will help us to understand the impact of L-cys on PL of ZnS QDs.

2. Experimental and computational methods

ZnAc₂·2H₂O, C₂H₅NS (TAA) and L-cys were analytical-grade and utilized without further refinement. For the uncoated ZnS, ZnAc₂·2H₂O and TAA were weighed (the molar ratio of ZnAc₂·2H₂O to TAA was 1:1) and blended with ethanol. After reacting in air at 90 °C for 3 h, the mixture was scattered into the distilled water and retrieved by centrifugation method. When the retrieved sediments were heated in vacuum at 60 °C for 5 h, ZnS samples were obtained. For L-cys capped ZnS QDs, after 0.5g as-grown ZnS QDs were washed with acetone solution, n-hexane (12 mL) and L-cys (the amount of L-cys was set on the basis of the quality ratio (L-cys:QDs = 0.4:0.5, 0.8:0.5, 1.2:0.5, 1.4:0.5 and 1.6:0.5) were mixed with QDs by grinding until n-hexane volatilized completely. The compound was dissolved in distilled water. After centrifuging, the sediments were heated in a drying oven under vacuum at 60 °C for 5 h. Thus, ZnS QDs with L-cys modification were obtained and labeled as L0.4, L0.8, L1.2, L1.4 and L1.6 corresponding to the dosage of L-cys was 0.4, 0.8, 1.2, 1.4 and 1.6 g, respectively.

X-ray powder diffraction (XRD) with Ni-filtered Cu Kα (Japan, XRD-6100, λ = 0.1541 nm) was used to measure the crystalline structure of the obtained products. The diameter, structure and surface morphology of products were analyzed by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) (JEM-2100). Fourier transform infrared (FTIR) spectroscopy (PerkinElmer) was used to characterized the surface properties of samples. A PL spectroscopy (Zolix, Omni PL-LF325) equipped with a He-Cd laser was used to record the emission spectra of all products at room temperature.

In order to complement the experimental data, vienna ab initio simulation program based on DFT
was used to calculate the band structure of the above four models [31]. Predew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) was used to represented the exchange and correlation potential [32]. The projector augmented wave (PAW) method was adopted to represent the reciprocities between the electrons and ions. The model of L-cys bonding with three low-Miller-index surfaces of ZnS (Fig. 1a), bulk ZnS (2×2×2 supercell, Fig. 1b), L-cys-ZnS (100) (L-Z(100), Fig. 1c), (110) (L-Z(110), Fig. 1d) and (111) (L-Z(111), Fig. 1e) surface (2×2×1 supercell) were created to study the impact of the shell on increasing PL of ZnS QDs. For the sake of avoiding the interactions between the neighboring layers in the z-direction, a supercell with 15 Å vacuum layers was introduced. A plane-wave cutoff of 380 eV was chosen and 2×2×2 and 2×2×1 \( k \) point mesh for bulk ZnS and L-cys bonding with ZnS was taken in the Brillouin zone, respectively.

Fig.1 Model of L-cys bonding with three surfaces of ZnS (a), super cell model of ZnS (b), super cell of L-cys bonding with ZnS (100) (c), (110) (d) and (111) (e) surface, successively.

3. Results and discussion

XRD techniques were used to analyze the crystal structure of ZnS sample without and with L-cys coated, as given in Fig. 2. The XRD results implied that all samples had a cubic zinc blende ZnS structure (JCPDS No. 65-0309). From Debey-Scherrer formula [33], the mean crystallite size of L-cys uncoated and coated QDs was obtained as 3.7, 4.2, 4.4, 4.9, 5.2 and 5.7 nm corresponding to ZnS, L0.4, L0.8, L1.2, L1.4 and L1.6, respectively, which indicated that the mean diameter of ZnS sample enlarged with the L-cys dosage increasing. The reason maybe that the surface defect state was improved by L-cys modification, which should reduce the surface energy of QDs. This process is helpful for the development of ZnS crystal nucleus.
In order to further clarify the crystal size, TEM and HRTEM measurements were carried out (shown in Fig. 3). It demonstrated that the particle size of sample L1.4 (L-cys:QDs = 1.4:0.5) was in the range of 4-6 nm, which agreed with the results of XRD analysis. The obtained spacing from the inset HRTEM (0.31 nm) was in accordance with the spacing of cubic zinc blende ZnS (111) planes (0.312 nm). In addition, it can be observed that sample L1.4 had a good dispersity.

![Fig. 3 TEM and HRTEM image of sample L1.4.](image)

The FTIR spectra of sample L1.4 and L-cys were given in Fig. 4a. In the FTIR spectral data of L-cys, the peaks that appeared at 638, 1064, 2551, 3425, 2979 and 3176 cm\(^{-1}\) related to \(\nu_{\text{C-S}}\), \(\nu_{\text{C-N}}\), \(\nu_{\text{S-H}}\), \(\nu_{\text{O-H}}\), and the symmetric and asymmetric stretching vibrations of \(\text{–CH}_2\) groups, respectively [34]. It can be seen that two absorption peaks around at 1587 and 1424 cm\(^{-1}\) related to the stretching vibration of \(\text{C=O}\) and \(\text{COO–}\) groups, respectively, which revealed that there were lots of carboxylic acid groups on the ZnS surface [35]. The results showed that the absorption peak (\(\nu_{\text{S-H}}\), 2551 cm\(^{-1}\)) cannot be found in sample L1.4, but other bands in the range of 500–1500 cm\(^{-1}\) can
be observed in both samples, which indicated that the disconnection of S-H bonds appeared, and the thiol group of L-cys was bonded with ZnS QDs and the –COOH group was remained on the outside surface of QDs. Moreover, two absorption peaks at 1061 cm⁻¹ (νC-N) and 864 cm⁻¹ (νC-H) can be found in both L-cys and sample L1.4, which implied the existent of L-cys in sample L1.4 [36].

From the digital photo of sample L1.4 (Fig. 4b) and ZnS (Fig. 4c) suspension in water, it was observed that there is sediment in the ZnS QDs suspension, but the sample L1.4 suspension showed excellent dispersibility because of the hydrophilic carboxylic acid group.

![Infrared spectra of L-cys and sample L1.4 (a), and the digital photo of L1.4 (b) and ZnS QDs (c) dispersed in water.]

The emission spectra of uncoated and coated samples at a laser excitation of 325 nm were given in Fig. 5. An obviously wide emission peak can be found within the scope of 350 to 650 nm, which originated from the trap-state emission in the ZnS QDs [37]. The PL data demonstrated that the coated layer helps to promote the luminescence of the as-grown sample, and the PL intensity of L-cys coated ZnS QDs achieved the maximum when L-cys:QDs = 1.4:0.5, since then began to reduce. To further determination of the effect of L-cys on promoting the PL, the energy band structures of all models were calculated and given in Fig. 6. The band gap of ZnS, L-Z(100), L-Z(110) and L-Z(111) was obtained as 2.10, 0.49, 1.98 and 2.10 eV, respectively. The position of the valence band of ZnS, L-Z(100), L-Z(110) and L-Z(111) was 0, 0.57, 0.09 and 0.46 eV, respectively, while the position of their conduction band was 2.10, 1.06, 2.07 and 2.56 eV, respectively. Basing on the relevant reports [38-40], ZnS@L-Z(100), ZnS@L-Z(110) and ZnS@L-Z(111) can form heterojunction and exhibit type-I, -I and -II behaviour, respectively (As shown in Fig. 6e). For ZnS@L-Z(100) and ZnS@L-Z(110) heterojunction, the conduction band and valence band of L-Z(100) and L-Z(110) should gather the photogenerated electrons and holes, respectively. For the type-II heterojunction, the photogenerated electrons and holes should move to the conduction band of ZnS and the valence band of L-Z(111), respectively. The results suggested that L-cys modification can help the isolation of electrons and holes on the surface after light radiation, and then the chance of nonradiative recombination on the surface should be reduced, which will enhance the emission intensity. Moreover, L-cys shell layer can lessen effectively the number of surface defect state. This process is good for the raising of PL intensity. Accordingly, the PL of sample L1.4 was 4.5 times more abundant than that of ZnS, but when the dosage ratio of L-cys:ZnS
QDs > 1.4:0.5, the PL began to decline. The reason maybe that the more L-cys use, the thicker capping layers obtain, and then the thicker the shell, the more it absorbs the emission light [25].

![Emission spectra of all samples](image_url)

**Fig.5** Emission spectra of all samples ($\lambda_{em}$=325 nm).

![Calculated band structures](image_url)

**Fig.6** Calculated band structures of ZnS (a), L-cys bonding with ZnS (100) (b), (110) (c) and (111) (d) surface. Diagram of the band edge positions after combination of L-cys and ZnS surfaces (e).

### 4. Conclusion

L-cys coated ZnS QDs with a mean diameter of 3.7-5.7 nm were successfully obtained in two-step method. The results displayed that the water-dispersity and PL intensity of ZnS QDs were furthered by modification with L-cys. When the mass ratio of L-cys to ZnS QDs was equal to 1.4:0.5, the emission intensity was 4.5 times as much as that of ZnS sample. The result of First-principles calculations implied that type-I and type-II heterojunction can be formed after L-cys modification, which should reduce the chance of the nonradiative recombination on the surface, and then increase the emission intensity.
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