Shell Thickness Dependence of Interparticle Energy Transfer in Core-Shell ZnSe/ZnS Quantum Dots Doping with Europium

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Abstract
Low-toxic core-shell ZnSe:Eu/ZnS quantum dots (QDs) were prepared through two steps in water solution: nucleation doping and epitaxial shell grown. The structural and morphological characteristics of ZnSe/ZnSe:Eu QDs with different shell thickness were explored by transmission electron microscopy (TEM) and X-ray diffraction (XRD) results. The characteristic photoluminescence (PL) intensity of Eu ions was enhanced whereas that of band-edge luminescence and defect-related luminescence of ZnSe QDs was decreased with increasing shell thickness. The transformation of PL intensity revealed an efficient energy transfer process between ZnSe and Eu. The PL intensity ratio of Eu ions (I613) to ZnSe QDs (I6) under different shell thickness was systemically analyzed by PL spectra and time–resolved PL spectra. The obtained results were in agreement with the theory analysis results by the kinetic theory of energy transfer, revealing that energy was transmitted in the form of dipole-electric dipole interaction. This particular method of adjusting luminous via changing the shell thickness can provide valuable insights towards the fundamental understanding and application of QDs in the field of optoelectronics.

Keywords: Core-shell quantum dots, Energy transfer, Shell thickness, Fluorescence lifetime

Background
Rare earth (RE) doped chalcogenide semiconductor quantum dots have received particular attention in the field of nanomaterials, due to their excellent photoelectric properties, such as multispectral luminescence, long fluorescent life, high luminous efficiency, low-gentle magnetic, etc. [1–4]. However, the absorption cross section of RE ions is very small (the order of magnitude is 10^-21 cm^-2), which leads to low luminescence efficiency [5]. Moreover, it is very difficult to directly stimulate transition of RE ions, since the f-f transition belongs to the parity forbidden transition according to the selection rule [6]. In order to overcome the above mentioned restrictions, significant research efforts have been devoted to the doping of RE ions into luminescent matrix materials. The matrix materials with large absorption cross-section can transfer energy to RE ions, so as to indirectly enhance their luminescence. This phenomenon is known as the “antenna effect” [7]. Various materials, such as fluorides, silicates, and chalcogenide semiconductor quantum dots are usually employed as matrix materials [8–14]. Among these, chalcogenide semiconductor quantum dots have some unique properties, such as quantum size effect, high fluorescence efficiency, large absorption cross section (1.1 × 10^-18 cm^-2), light stability, rendering them as excellent candidate materials [15–18]. Up to now, the research efforts on RE doping in chalcogenide semiconductor quantum dots were mainly focused on tuning luminescence wavelength and improving PL efficiency, by adjusting doping concentration, reaction time, and other experimental parameters [19–21]. In the research of dopant QDs, energy transfer was usually a means of explaining spectral phenomena, but the intrinsic mechanism of energy transfer was rarely explained.

In view of the above perspectives, the PL characteristics and intrinsic energy transfer mechanism of core-shell ZnSe:Eu/ZnS QDs were thoroughly explored in the present work. The luminescence spectra of the ZnSe host materials and Eu ions were investigated by controlling shell thickness. The mechanism of energy transfer
between Eu ions and ZnSe/ZnS core-shell quantum dots was systematically analyzed by time-resolved fluorescence spectroscopy and energy transfer kinetic theory.

**Methods/Experimental**

In this paper, ZnSe:Eu/ZnS core-shell quantum dots were prepared through nucleation doping and epitaxial growth method. The detailed preparation process was described as follows: the mixture of zinc nitrate hexahydrate (Zn(NO$_3$)$_2$.6H$_2$O), europium(III) nitrate hexahydrate (Eu(NO$_3$)$_3$.6H$_2$O), and 3-Mercaptopropionic acid (MPA) with a molar ratio of Zn$^{2+}$/Eu/MPA = 1:0.06:20 prepared (NO$_3$)$_2$.6H$_2$O), and 3-Mercaptopropionic acid(MPA) with

**Results and Discussion**

Figure 1a–o representatively shows the TEM results for core ZnSe:Eu QDs and core-shell ZnSe:Eu/ZnS QDs with different shell thickness. From the Fig. 1a–c, we can see that the shape of ZnSe:Eu QDs are regular spherical, and the average size is 2.7 nm. The high-resolution transmission electron microscopy (HRTEM) demonstrates the excellent crystallinity of the ZnSe:Eu QDs.

In particular, when ZnSe:Eu QDs are epitaxial coated with ZnS shell, the lattice constants of the two counterparts are not equal and the lattice continuity across the interface is destroyed, resulting in lattice mismatch. Because of lattice mismatch, ZnSe suffered compressive stress at the interface and ZnS is subjected to tensile stress, and the average lattice constant changed [26]. Consequently, the induced stress modifies the energy level structure of the core-shell nanoparticles, which in turn alters the electron energy level structure in the nanocrystalline particles. Three possible steps are considered for exciton recombination process: (i) radiation recombination of excitons in host materials (including the edge emission and defect emission of ZnSe); (ii) non-radiation recombination through heat transfer loss; (iii) energy transfer between ZnSe host and Eu ions, which enhanced PL intensity of Eu ions. These three steps competed each other, resulting in the simultaneously appearance of three PL peaks as shown in Fig. 2a. The two types of fluorescence transfer part of energy to the adjacent Eu ions during radiation recombination process, which resulted in
Fig. 1 TEM images and histograms of the measured particle sizes of ZnSe:Eu QDs (a, b) and overcoated with 1 ML (d, e), 2 ML (g, h), 3 ML (j, k), and 5 ML (m, n) of the ZnS shell, respectively. Cryo-HRTEM of core ZnSe:Eu (c) images and the corresponding core-shell ZnSe:Eu /ZnS QDs with 1 ML (f), 2 ML (i), 3 ML (l), 5 ML (o) shell, respectively.
electrons transitions in Eu ions from $^7F_0$ state to $^5D_0$ state [27], as shown in Fig. 3.

The time-resolved PL spectra of ZnSe:Eu/ZnS core-shell QDs is an important means to detect energy transfer between them [28]. The fluorescence lifetime of the characteristic luminescence peak at 613 nm of Eu and that of the band-edge luminescence peak at 406 nm of ZnSe with different ZnS shell thickness is shown in Fig. 4. With the increase of ZnS shell thickness, the average lifetime of donor ZnSe QDs decreases exponentially as fast-acting energy transfer for enhanced stress in core-shell structure. Concomitantly, the acceptor Eu average lifetime increases as it receives transferred photon energy.

According to the kinetic theory of energy transfer, the ratio of ZnSe band edge PL intensity ($I_B$) to that of Eu ion ($I_{613}$) as a function of the ZnS shell thickness can be calculated by time-resolved PL spectra [29]. Under steady-state excitation conditions, the energy transfer rate for ZnSe-Eu can be expressed according to Eq. 1:

$$W_{\text{ZnSe-Eu}} = \frac{n_2}{\tau_2}$$

where $W_{\text{ZnSe-Eu}}$ is the energy transfer rate of ZnSe-Eu; $\tau_2$ is the lifetime of Eu ions ($I_{613}$); $n_1$ and $n_2$ are the number of excited ions of ZnSe and Eu ion level, respectively. The macroscopic energy transfer rate can be expressed as follows:

$$W_{\text{ZnSe-Eu}} = \frac{1}{\tau_1} - \frac{1}{\tau_0}$$

where $\tau_0$ is the lifetime of the bare ZnSe QDs when the ZnS shell thickness is 0 ML and $\tau_1$ is the lifetime of ZnSe band edges ($I_B$). The ratio between band-edge emission intensity ($I_B$) of ZnSe QDs to that of Eu ions ($I_{613}$) can be expressed as follows:

$$\frac{\gamma_2}{\gamma_1} W_{\text{ZnSe-Eu}} = \frac{I_{613}}{I_B}$$

where $\gamma_1$ and $\gamma_2$ are the emissive coefficients.

Comparing the experimental ratio of $I_{613}/I_B$ (red bar graph) with the theoretical results (black bar graph), we can conclude that the ratio calculated by the
luminescence kinetics model agree well with the experimental results, as shown in Fig. 5. It also demonstrates the energy transfer efficiency increased with the increase of shell thickness.

No radiation energy transfer mainly takes place via the interaction between multipolar moments. When the distance between the host and the guest is relatively short, the energy can be transferred from the host (donor: ZnSe) to the guest (acceptor: Eu) through multipole interaction [30]. The mechanism of energy transfer between donor and acceptor can be corroborated by considering the fluorescence intensity and lifetime of the donor and the acceptor. The fluorescence lifetime of the multipole moment can be expressed according to Eq. (4):

\[
\phi(t) = \exp \left[ -\frac{t}{\tau_0} - T \left( 1 - \frac{3}{s} \frac{c}{c_0} \left( \frac{t}{\tau_0} \right)^s \right) \right]
\]

where \(\tau_0\) is the fluorescence lifetime of the donor without dopant, \(c\) is the doping concentration of acceptor, \(c_0\) is the critical concentration related to critical distance \(c_0 = 3 / (4\pi R_0^3)\). Different \(s\) values stand for the interaction of different multipolar moments [31]. It corresponds to electric dipole-electric dipole interaction for \(s = 6\), dipole-quadrupole interaction for \(s = 8\), and quadrupole-quadrupole interaction for \(s = 10\), respectively. The fitting results for different \(s\) values are depicted in Fig. 6. The ratio of band-edge luminescence intensity and fluorescence lifetime is well matched with the fitting results for \(s = 6\), which indicates the existence of energy transfer between the donor of ZnSe and Eu acceptor by electric dipole-electric dipole mode. These two of the interactions for cross relaxation are electrostatic in origin.

Conclusions
The ZnSe:Eu/ZnS (QDs) were prepared by wet chemical method via nuclear doping followed by epitaxial ZnS shell growth. The morphology and structure of core-shell ZnSe:Eu/ZnS QDs were clearly revealed by TEM and XRD results. The photoluminescence (PL) spectra of ZnSe:Eu/ZnS QDs with different thickness of ZnS shell showed that the PL intensity of the Eu characteristic luminescence peak increased while that of characteristic luminescence and defect luminescence of ZnSe decreased, illustrating an effective energy transfer between ZnSe and...
Eu. The intrinsic mechanism of energy transfer with different ZnS shell thickness was systematically investigated through time-resolved spectra and energy transfer dynamics theory. The results revealed that energy was transmitted in the form of dipole-electric dipole interaction.

**Abbreviations**

$\lambda_{PL}$: The PL intensity integral of the Eu ion; $I_{ZnSe}$: The band edge PL intensity integral of ZnSe; $I_{PL}$: The defect-related luminescence intensity integral of ZnSe; PL: Photoluminescence; QDs: Quantum dots; TEM: Transmission electron microscopy; XRD: X-ray diffraction

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**Declarations**

This study has nothing to do with human participants or health-related outcomes.

**Authors’ Contributions**

LN designed and conducted the experiments and analyses, and drafted the manuscript. LSX analyzed the data and supervised this study. WCF and LJ conceived the project, organized the paper, and edited the manuscript. All authors read and approved the manuscript.

**Competing Interests**

The authors declare that they have no competing interests.

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