

Influence of the second shell layer (TOPO, HDA) on the optical properties of CdSe/ZnS nanocrystal powder

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CdSe/ZnS nanocrystal powder covered with an additional cap layer (II-shell) of hexadecylamine (HDA) or tri-n-octylphosphine oxide (TOPO) has been investigated by using photoluminescence (PL) and total photoluminescence excitation (TPLE) spectroscopy. Depending on II-shell composition, different emission properties of the system have been observed. Strong emission bands at 2.00 eV and 1.95 eV related to nanocrystalline CdSe core recombination have been observed for TOPO and HDA-CdSe/ZnS nanocrystals, respectively. In both cases, weak emission bands centered at 3.5 and 2.8 eV have also been found. Moreover, in the case of TOPO II-shell, emission band at 1.65 eV related to defect state recombination has been observed. In both cases, similar absorption properties have been found, indicating that II-shell composition does not change nanocrystal absorption properties in an efficient way.

Keywords: nanocrystals, photoluminescence, CdSe/ZnS, HDA, TOPO.

1. Introduction

Nanocrystals of II–VI semiconductors (for example, CdS or CdSe), in a size range of a few nanometers, reveal original optical properties due to quantum exciton confinement [1, 2]. The optical emission and absorption can be tuned across the visible spectrum by varying the size of nanocrystals [3–5]. This makes these materials attractive for many applications, including biological labeling [6], light-emitting devices [7, 8], and optoelectronics, where nanocrystalline properties are widely used [9, 10].

Numerous investigations regarding the optical properties of these nanocrystals have been reported [11–16]. It has been shown that covering the nanocrystals with higher band gap inorganic semiconductor materials (for example, ZnS) can substantially improve their emission properties. This may result from passivating surface nonradiative recombination sites and efficient localization of the wave function inside the core. It is also very common to cover such a core/shell nanocrystals with

the additional cap layer of organic ligand tri-*n*-octylphosphine oxide (TOPO) or amines. This coverage ensures the solubility of the nanocrystals in toluene and prevents aggregation. Although CdSe/ZnS is a well characterized semiconductor QD system, there is still a lack of optical investigations into the influence of the second shell (II-shell) on the optical properties of the core.

In this paper, photoluminescence (PL) and total photoluminescence excitation (TPLE) investigation of optical properties of CdSe/ZnS nanocrystals, covered with additional cap layer of TOPO or hexadecylamine (HDA) will be presented.

2. Experimental details

The free standing nanocrystals (nanocrystalline powder containing nanocrystals without any matrix, surrounded by air and closed in a quartz chamber) were investigated by using photoluminescence (PL) and total photoluminescence excitation (TPLE) spectroscopy (where the full PL spectra are collected for different excitation wavelengths in the broad spectral range). The CdSe/ZnS nanocrystals were additionally covered with a cap layer of tri-*n*-octylphosphine oxide (TOPO) and hexadecylamine (HDA). All samples were produced by the Nanoco Company, and the composition of additional cap layers as well as nanocrystal production method are protected by patent.

The room temperature PL and TPLE spectra were obtained by exciting the samples with a xenon lamp combined with Triax 180 monochromator. For our measurements the HR4000 Ocean Optics Spectrometer was used as a detection system.

3. Results and discussion

Figure 1 shows photoluminescence spectra obtained for CdSe/ZnS nanocrystalline powder covered with an additional cap layer (TOPO or HDA) at a 300 nm excitation wavelength. Strong, visible emission bands at 2.00 and 1.95 eV have been observed for structures with TOPO and HDA II-shell layers, respectively. It has been found that different II-shell layers influence in different way the optical properties of the structures under investigation. In the case of TOPO layer, there is an additional broad emission band centered at ~1.68 eV. This is probably related to recombination from not completely passivated defect states of the CdSe core. The intensity of this band is significantly lower for the nanocrystals covered with HDA, indicating better optical properties in this kind of structures.

Apart from that, for all the samples, quantum size effect has been observed (emission for bulk CdSe takes place at ~1.74 eV, while in Fig. 1 it is shifted towards shorter wavelengths).

Figure 1 shows additionally integrated photoluminescence intensity for all samples as a function of the excitation wavelength. It can be seen that the spectra obtained do

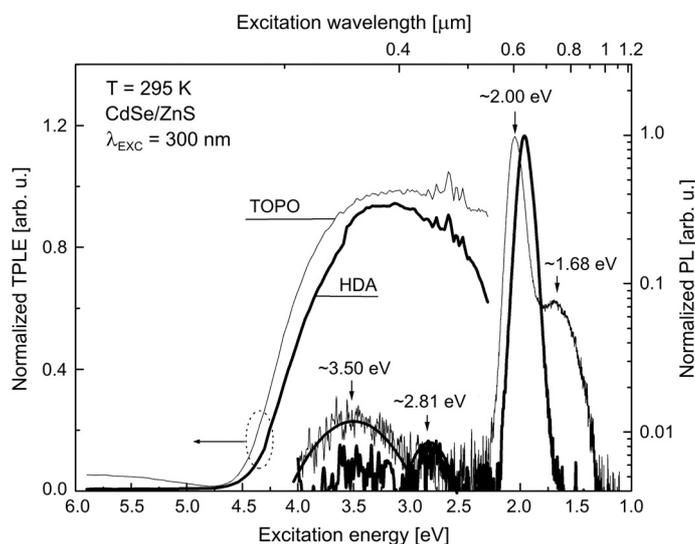


Fig. 1. Total photoluminescence excitation spectra (left axis) and photoluminescence spectra (right axis) obtained for CdSe/ZnS nanocrystalline powder covered with additional cap layer of TOPO or HDA in the broad energy range.

not differ considerably in all the cases. This result indicates that absorption mechanism in the spectral range under investigation is similar for both structures.

It can also be seen that both TPLE spectra have a complex structure around 2.5 eV. This is due to the fact that for energy range of 2.0–3.0 eV excitation of electron–hole pairs occurs in the nanocrystal core, in which electron and hole states are quantized [17, 18].

Moreover, Fig. 1 shows that the absorption in energy range of 3.0–3.5 eV does not depend on the excitation wavelength. It can also be seen that for all the samples there is an evident absorption edge around 4.0 eV, above which TPLE signal rapidly disappears. It has been shown that above 4.0 eV excitation in ZnS layer is also possible [19]. When the excitation energy is higher than 4.0 eV, electron–hole pairs could be created in the ZnS shell and therefore can *i*) recombine radiatively, *ii*) recombine nonradiatively to the defect states and then radiatively, or *iii*) both carriers can recombine nonradiatively into CdSe core ground states and then radiatively. On the other hand, ZnS surface very often contains many defect states, therefore nonradiative recombination becomes possible and TPLE signal would fiercely decrease. This has been discussed in more detail in our previous paper [20], where it has been shown that defect states in the ZnS shell and the ZnS shell itself may be the source of new nonradiative or radiative recombination channels in the CdSe/ZnS nanocrystals and lead to a decrease of the quantum yield of composite particles.

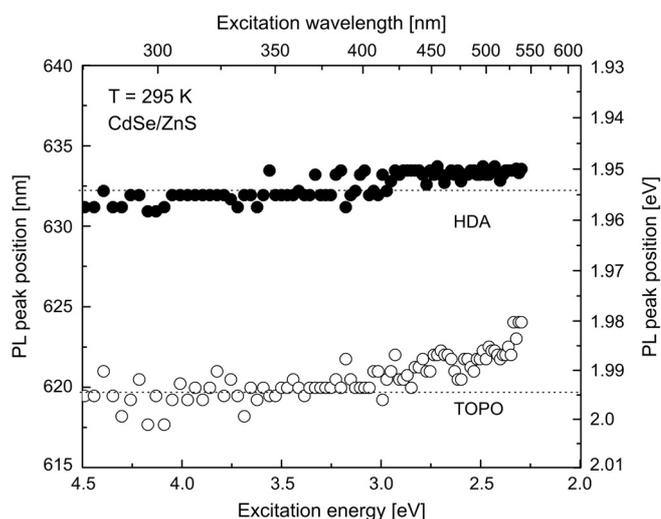


Fig. 2. Photoluminescence peak position as a function of excitation wavelength obtained for CdSe/ZnS nanocrystalline powder covered with additional cap layer of TOPO or HDA.

In Figure 1, it can also be seen that there are two additional bands centered at 2.81 eV and 3.50 eV, which appear when nanocrystals are excited by a 300 nm wavelength. These transitions can be attributed to the transition from the ZnS shell layer and transition related to the defect states in the ZnS/HDA interface.

Moreover, it has been found that the shape and PL peak position depend on excitation energy. As can be seen in Fig. 2, the position of photoluminescence peak shifts towards lower energies, while decreasing the excitation energies, both for TOPO and HDA cap layers. This result could be interpreted as follows. Observed in our experiment, the PL emission band is a superposition of many spectra differing in size or shell thickness of nanocrystals. For the excitation energy greater than band-gap of the smallest nanocrystal, all nanocrystals are excited and in consequence, all of them give input in the PL spectrum. With the excitation energies decreasing, due to quantum size effect, only bigger nanocrystals with smaller band-gap can be excited. Then the resultant emission band is observed to shift towards shorter wavelengths. Because smaller shift means smaller size/shell thickness distribution, from Fig. 2 it can be concluded that homogeneity of samples with HDA cap layer is greater than in the case of TOPO.

4. Conclusions

It has been shown that stoichiometry of the II-shell strongly affects the optical properties of CdSe/ZnS nanocrystals. It has also been found that by using HDA cap

layer, passivation of the defect states is more efficient and the nanocrystal size/shell thickness distribution are narrower compared to TOPO II-shell.

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