Optical Analysis of a series of Size and Shape-controlled Type-II CdTe/CdSe/CdTe Heterostructure Nanorods

Hongming Zhao1,3, Bonil Koo2, J.L. Movilla4, Dongmin Chen3, Brian A. Korgel2 and Kuntheak Kheng1

1Nanophysics and Semiconductor Group, CEA/CNRS/Université Joseph Fourier, Institut Néel, 38054 Grenoble Cedex 9, France
2Department of Chemical Engineering, Center for Nano- and Molecular Science and Technology, and Texas Materials Institute, University of Texas, Austin, TX 78712, USA
3Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, 100190 Beijing, P.R. China
4Department of Physical and Analytical Chemistry, University Jaume-I, E-12080 Castelló, Spain

Email : kuntheak.kheng@ujf-grenoble.fr

Abstract. Two series of size and shape-controlled type-II CdTe/CdSe/CdTe heterostructure nanorods with different geometrical structures were prepared by the colloidal sequential reactant injection technique. The samples, including pure CdSe seeds, were optically analysed by steady state and time resolved photoluminescence spectra. The experimental results demonstrate that the energy and lifetime of the photoluminescence from charge-separated band structure can be tuned by the nature of nanorods’ band edges in both “linear” and “core-shell” heterostructure nanorods. But between different groups of nanorod samples, the spectral properties show different variation tendencies with the increasing CdTe tip. As one possible explanation, the compensation between the variations of kinetic and Coulomb contributions was discussed by numerical calculations based on the effective mass and envelope function approximations.

1. Introduction
The type-II CdTe/CdSe nanocrystals have been extensively studied for potential applications in optoelectronic devices and for their novel electronic and optical properties that come from quantum confinement in their unique structure different from type-I nanocrystals [1, 2, 3]. At the interface between CdSe and CdTe segments, the band edges have a staggered type-II alignment. The conduction and valence band energies within the CdSe segment are respectively lower than the conduction and valence band energies in CdTe, as showed in Figure1.(a). After the photo-excitation, it is inclined to give a spatial separation of confined holes and electrons in type-II band alignment, making easier to
harvest the photo-generated carrier. This makes CdTe/CdSe heterostructures an attractive candidate for the fabrication of solar cells [4].

Recent series of works described the progress of synthesis and characterization of nonspherical CdTe/CdSe heterostructure [5, 6, 7]. Comparing to the spherical nanocrystals, the optical and electronic properties of size- and shape-controlled nonspherical nanorods can be manipulated more easily. Due to the tunable properties, these heterostructures nanorods provide exciting opportunities for fundamental research of nanostructures and potential optoelectronic device application. The basic optical properties of CdTe/CdSe/CdTe heterostructure nanorods have been obtained by recent studies [7]. It was found that the PL spectra at low temperature originated from two different optical transitions: the direct (type-I) radiative recombination of CdSe and the red-shifted radiation from type-II transition due to an electron in CdSe segment and a hole in CdTe. For further understanding of the characteristic of indirect type-II transition in this system, two different geometrical structure of CdTe/CdSe/CdTe heterostructures nanorods were designed and synthesized.

2. Experiment

Two series of samples (A and B) have been synthesized. From a same CdSe seed (sample N1), increasing CdTe tips at both ends are grown (samples N2 to N5). The nanorods of series A are perfect linear heterostructures, while the nanorods of series B have an additional core-shell heterostructure interface, see Figure1.(b). The CdTe/CdSe/CdTe heterostructure nanorods were synthesized by the colloidal sequential reactant injection technique [5, 6]. Firstly, a Cd-TDPA complex [8], which is necessary for nanorod formation, was prepared and degassing. Then, a mixture of 0.856 g of Cd-TDPA complex and 1.1436 g of TOPO was degassed in the reaction flask for one hour and heated to 320 °C under nitrogen. A selenium precursor reactant solution was prepared by dissolving 0.0316 g of Se in a mixture of 0.117 mL of TBP, 0.8705 mL of TOP, and 0.1735 mL of toluene at 120 °C. The tellurium reactant solution was made under the same condition except with an increased amount (1.25 mL) of TOP to lower the solution viscosity for easy injection through a syringe pump. The selenium precursor was rapidly injected into the mixture of Cd-TDPA and TOPO at 320 °C. The temperature was then immediately decreased to 275 °C to promote the formation of relatively high aspect ratio CdSe nanorods [8]. After heating for 15 minutes, the tellurium precursor was injected by syringe pump for 7.5 minutes at 250 °C, which yields linear CdTe/CdSe/CdTe heterojunction nanorods. In contrast, to make core-shell type heterojunction nanorods, the reaction solution was heated to 275 °C and then the tellurium precursor was injected at the same injection rate. During Te-injection, nanorods were removed from solution at different times in ~0.3 mL aliquots for characterization.

Careful size calculations based on the TEM micrographs give the mean diameter and length of both the seed CdSe (named N1) and the CdTe/CdSe/CdTe heterostructure nanorods (named N2, N3, N4 and N5). The serial number and corresponding size of samples-A and -B are presented in Table 1. The standard deviation of the size ranged between 10 and 15% for all samples.

| Serial number and corresponding size of samples-A and -B. |
|-----------------|---------|---------|---------|---------|
| Samples-A       | N1(seed)| N2      | N3      | N4      | N5      |
| Diameter(nm)    | 3.48    | 3.50    | 3.50    | 3.50    | 3.51    |
| Length(nm)      | 20.3    | 25.3    | 32.1    | 37.9    | 40.1    |
| Samples-B       | N1(seed)| N2      | N3      | N4      | N5      |
| Diameter(nm)    | 3.74    | 3.79    | 3.77    | 3.81    | 4.16    |
| Length(nm)      | 25      | 28.1    | 37.4    | 41.7    | 50.7    |

For samples-A, the diameter from N2 to N5 keeps at about 3.5nm and they are considered as “linear” heterostructures nanorods. But the difference of diameters between different samples in samples-B is out of just error range of measurement, meaning that there is additional CdTe growth as a shell. They are “core-shell” heterostructure nanorods.
Steady-state photoluminescence (PL) spectra have been measured (using the 448nm line of an Argon ion laser) on these samples to investigate the competition between emissions from type-I and type-II band structure. To confirm the long lifetime expected for the type-II transition and characterize the relationship between the emission lifetime and wavelength in PL of CdTe/CdSe/CdTe heterostructure nanorods, time resolved PL (TRPL) experiments were carried using a frequency doubled, pulsed Ti-sapphire laser with a pulse interval modulation system which can adjust the interval of laser pulse (“time window”) in a large range.

3. Results and Discussions

Figure1.(a) Type-II band alignment at the interface between CdSe and CdTe; (b) The geometrical structure of samples-A and -B; (c) PL of CdSe seed (N1) and samples-A (from N2 to N5); (d) PL of CdSe seed (N1) and samples-B (from N2 to N5); All the data were obtained at 5K.

Figure1.(c) and (d) shows the -PL spectra at 5K of pure CdSe seeds (N1), the CdTe/CdSe/CdTe heterostructure nanorods (N2-N5) from samples-A and -B respectively. The type-I direct transition line is observed at about 600nm of N1 samples (pure CdSe nanorod seed). The PL spectra of CdTe/CdSe/CdTe heterostructure nanorods (N2-N5) show an additional broad PL peaks (700-850nm) whose intensity increases with the length of the CdTe tips. This broad peak is attributed to type-II emission [9]. Due to the weak overlap of wavefunction within the spatially separated electrons and holes in type-II structure [3], a long lifetime of type-II emission in samples-A and -B nanorods is expected. The TRPL was carried out to confirm it. We show the results for each series A and B, in samples N3 (Fig. 2) because both the type-I (at about 600nm) and the type-II (about 770nm) transitions have substantial intensity in the same sample. We found indeed a very long lifetime which is more than 1000ns for the indirect emission at about 770nm as compared to the 4.0 ns (measured with a more accurate time scale) decay time of the CdSe direct emission at 600nm, as shown in Figure2.

As presented in Figure1.(c) and (d), for samples-B, with the increasing length of CdTe tip from nanorods N2 to N5, the intensity of additional broad PL peaks increased with a red shift of the wavelength of peak from 790nm to 850nm. That is, bigger CdTe tips (act as shells) had lower energy.
gap. But for A samples, the broad emission peaks (~770nm) in happened all at the same position. In order to confirm theoretically the possible interpretations, we carried out numerical calculations based on the effective mass and envelope function approximations to describe the one-band electron and hole single-particle Hamiltonians, followed by a full configuration-interaction scheme to include the electron-hole Coulomb attraction (see e.g. [12] for details).

The results of the simulations were consistent with the experimental observations. For samples-A, the “linear” heterostructure nanorods, except for very low CdTe injection, the type-II transition energy tends rapidly to a constant value as the CdTe length increases, which is due to a compensation between the variations of kinetic and Coulomb contributions. Thus, as the length of the CdTe tip increases, the hole kinetic energy is relaxed, favoring a decrease of the gap energy. However, such decrease is compensated by the effect of a less effective Coulomb stabilization of the exciton yielded by the increase of the mean distance between electron and hole. But the compensation is not present in samples-B. The red shift of the type-II emission as the CdTe injection increases is ascribed mainly to the increase of the rod width (which is produced because of the growth of the CdTe shell), and not because of the increase in length. The reason is that, due to the large anisotropy of the confining potentials, the (strong) lateral confinement is much more effective than the longitudinal (growth direction) confinement and, as a consequence, now both electron and hole undergo a large relaxation of the kinetic energy which is no longer compensated by Coulomb contributions.

4. Conclusions

The optical analyses of a series of type-II CdTe/CdSe/CdTe heterostructures nanorods with different geometrical structures by steady state PL and TRPL was carried out. The size dependent wavelength shift of PL spectra at 5K shows the transfer of charge carries recombination from type-I (CdSe) to type-II transition (CdSe/CdTe) and the competition between the two routes of recombination. The origin of the apparently different behavior of samples-A and -B is the large anisotropy of the rod shape, which makes the electron and hole energy much more sensitive to changes in the (strong) lateral confinement than in the (weak) longitudinal one. These results and tentative conclusions, which are described by the numerical calculations, should help to shed light on our understanding of the type-II band alignment in CdTe/CdSe/CdTe heterostructures nanorods. Further experiments and theoretical calculation about the optical properties in this system are in progress.

Acknowledgments

This work was support by China Scholarship Council (CSC, File No.2008491036). We would like to thank Dr. Joël BLEUSE for the critical assistance and discussions of TRPL measurements.

References

[1] Kim S, Fisher B, Eisier H J and Bawendi M 2003 J. Am. Chem. Soc. 125 11466.
[2] Sandeep Kumar, Marcus Jones, Shun S. Lo, and Gregory D. Scholes 2007 Small 3, 9, 1633 – 1639.
[3] Wang C H, Chen T T, Chen Y F, Ho M L, Lai C W and Chou P T 2008 Nanotechnology 19 115702.
[4] Gur I, Fromer N A, Geier M L and Alivisatos A P 2005 Science 310 462.
[5] Shieh F, Saunders A E and Korgel B A 2005 J. Phys. Chem. B 109 (18), 8538-8542.
[6] Koo B, Korgel B A 2008 Nano Lett. 8, 8, 2490–2496.
[7] Saunders A E, Koo B, Wang X, Shih C K and Korgel B A 2008 ChemPhysChem 9,1158-1163.
[8] Peng Z A, Peng X J 2002 Am. Chem. Soc 124, 3343.
[9] Brus L 1986 J. Phys. Chem 90 2555.
[10] Efros Al L and Efros A L 1982 Soviet Phys. Semicond 16 772.
[11] Alivisatos A P 1996 J. Phys. Chem 100, 13226-13239.
[12] J.L. Movilla, J.I. Climente, J. Planelles 2010 Computer Physics Communications 181 92–98.