Optical Characterization of Type-II CdTe/CdSe/CdTe Heterostructure Nanorods

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Abstract. The optical characteristics of an indirect type II transition in a series of size and shape-controlled linear CdTe/CdSe/CdTe heterostructure nanorods was studied by steady state and time resolved photoluminescence spectra. The energy and lifetime of the photoluminescence from the charge-separated band structure can be tuned by the band edges of the nanorods. Our results show a size-dependent transition from a type I direct transition (CdSe$\sim$600 nm) to an indirect type II transition (CdSe/CdTe). The heterostructure nanorod geometry and dimensions that induce type-II charge separation without type-I recombination were determined. The indirect type II transition at 5 K exhibited a long PL decay time, of more than 1000 nanoseconds, that increased with PL wavelength, which can be rationalized by the changing of wavefunction overlap of electrons and holes induced by the quantum confinement effect in type-II band structure.

1. Introduction
In recent years, type-II CdTe/CdSe nanocrystals have received tremendous attention because of the distinctive optical and electronic properties that come from quantum confinement in their unique structure \cite{1, 2, 3}. Particularly, the photo-induced spatial separation of confined holes and electrons in type-II band alignment makes them an attractive candidate for the fabrication of solar cells \cite{4}. Recently, the synthesis and characterization of nonspherical CdTe/CdSe/CdTe heterostructure nanorods has been described \cite{5, 6, 7}. Comparing to spherical nanocrystals, the optical and electronic properties of size- and shape-controlled linear nanorods can be manipulated more easily. Due to their tunable properties, such as the photoinduced charge separation and long emission lifetime \cite{2}, these nonspherical heterostructures provide exciting opportunities for fundamental research of nanostructures and potential optoelectronic device application.
The band edges have a staggered type-II alignment at the interface between CdSe and CdTe segments in linear CdTe/CdSe/CdTe heterostructure nanorods. The conduction and valence band energies within the CdSe segment are respectively lower energy than the conduction and valence band energies in CdTe, as shown in Figure 1(a). After photoexcitation, there is a spatial separation of charge. The basic optical properties of CdTe/CdSe/CdTe heterostructure nanorods, including the absorbance spectrum and temperature-dependence of the PL spectra, have been obtained by recent studies [7]. It was found that the PL spectra at low temperature originated from two different excited emissions: the 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. To further understand the characteristics of the indirect type II transition (CdSe/CdTe) in nanorods, a series of linear CdTe/CdSe/CdTe heterostructures were prepared. In our paper, steady-state PL spectra were performed on these samples to investigate the size-dependent transition of the emission from type-I to type-II. Based on the results of these measurements, a characteristic geometry and dimensions for charge separation in this system has been identified. Time resolved PL (TRPL) experiments were carried out to confirm the long lifetime expected for the type-II transition and characterize the relationship between the PL emission lifetime and peak wavelength of CdTe/CdSe/CdTe heterostructure nanorods.

2. Experiment

2.1. Sample Synthesis

The CdTe/CdSe/CdTe heterostructure nanorods were synthesized by the colloidal sequential reactant injection technique [5, 6]. A Cd-TDPA complex was prepared as previously described [8]. On a Schlenk line, 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 conditions, 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 250 °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 275 °C. During Te-injection, nanorods were removed from solution at different times in ~0.3 mL aliquots for characterization.

Careful size calculations based on the transmission electron microscopy (TEM) images provided 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 are presented in Table 1. The standard deviation of the size ranged between 10 and 15% for all samples.

| Samples | 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 |

The slight increase in nanorod diameter upon CdTe addition to the CdSe nanorods indicates that there is some additional CdTe growth as a shell. This series of samples are linear and core-shell type heterostructure nanorods, see Figure 1(b). They are named as “core-shell nanorods”.

2.2. Optical Measurement

Steady state PL measurements were carried out using an Argon ion laser with a wavelength of 488 nm as the excitation source. The PL spectra were analyzed spectrally by a Jobin Yvon THR1000 monochromator, which consists of a reflective grating with 600 (for wide spectral ranges) lines/mm,
and detected by a charged coupled device (CCD). Time-resolved photoluminescence (TRPL) measurements were performed with a frequency doubled, pulsed Ti-sapphire laser with a pulse interval modulation system, which can adjust the interval of laser pulse (“time window”) over large range, as the excitation source. In our experiments, it is a 440 nm laser with 1000 ns or 10 ns pulse interval. Emission decay passed through a monochromator and was then detected by a streak camera. To ensure that the triangular voltage of streak camera is released exactly when the signal arrives at the entrance of the camera, the laser pulse was split by a beam splitter and one of the two resulting pulses was used as a trigger signal.

3. Results and Discussions

Figure 1(c) shows the steady state PL spectra at 5 K for the CdTe/CdSe/CdTe heterostructure “core-shell nanorods”. As compared to a type-I direct transition line at about 600 nm of N1 sample (pure CdSe nanorod seed), the PL intensity of N2 and N3 shows a shift from the 600 nm CdSe peak to an additional broad PL peak at about 750 nm. With the increasing length of the CdTe segment at the tips of the nanorods, from N4 to N5, the intensity of the additional broad PL peaks increased with a red shift of the wavelength of peak from 790 nm to 850 nm. The additional broad PL arises from type-II emission [1]. The size-dependent energy level shift induced by the changing of quantum confinement effect [9, 10, 11] is a manifestation of the competition between the recombination of exciton in CdSe core (type-I emission) and spatially separated charges across the CdTe/CdSe interface in these heterostructure nanorods. Owing to the fact that there is no type-I emission in N4 and N5 of “core-shell nanorods”, their geometry and dimensions will be the suitable ones for the charge separation in this system.

Due to the weak electron and hole wavefunction overlap arising from their spatial separation due to the type-II band alignment [3], a long lifetime of type II emission in CdTe/CdSe/CdTe heterostructure nanorods is expected. TRPL was carried out to confirm it. Spectra of “core-shell nanorods” N3 were taken as an example, owing to the observation both type-I (about 600 nm) and type-II (about 750 nm)
transitions. We found that indeed a very long lifetime, of more than 1000 ns, was observed for the indirect emission at about 750 nm. In contrast, the decay time of the CdSe direct emission at 600 nm was only 4.0 ns (measured with a more accurate time scale), as shown in the inset of Figure 2. In order to characterize the effect of the type-II band alignment on the decay dynamics of the photoinduced, spatially separated charge in CdTe/CdSe/CdTe heterostructure nanorods, the relationship between the emission lifetime and detected PL wavelength at 5 K was studied and is presented in Figure 2. The emission lifetime increases as the detected PL wavelength of the type-II emission increases (decreasing photon energy). This behavior can be attributed to the quantum confinement effect in type-II band alignment. Different from the type-I band alignment, in a type-II band structure, the photo-induced electrons and holes are confined in different materials at the interface of CdTe/CdSe, such as in Figure 1(a). Comparing to the shorter PL wavelength in type-II emission, the longer one corresponds to less quantum confinement, resulting in less overlap of the electron and hole wavefunctions. Since the radiative decay rate of photo-excited carriers is proportional to the square of wavefunction overlap, the relationship between the emission lifetime and detected PL wavelength is easy to be understood.

4. Conclusions

We have studied the optical characterization of a series of linear type-II CdTe/CdSe/CdTe heterostructure nanorods by steady state PL and TRPL. The size dependent wavelength shift of PL spectra at 5 K shows that there is a transition in charge carrier recombination from type-I (CdSe) to type-II transition (CdSe/CdTe) with nanorod size due to the competition between the two recombination pathways. We found that the geometry and dimensions of “core-shell nanorods” N4 and N5 should be suitable for the type-II spatial separation of photo-induced charge without type-I recombination. The weak wavefunction overlap of specially separated electrons and holes was verified by the long lifetime (more than 1000 ns) of type-II emission in PL spectra of heterostructures nanorods. Finally, we investigated the emission lifetime at different detected PL wavelength in type-II region. These results can be well explained by the quantum confinement effect in type-II band alignment. Further experiments about the decay dynamics in this system and the relationships among PL intensities and PL decay time are currently underway.

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