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Energy Transfer among CdTe tetrapod nanocrystals

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Abstract. A transmission electron microscope image of a mixture of two different tetrapod nanocyrstals (TNCs) with different pods' length (11 nm and 14 nm), revealed the existence of a bundled arrangement with inter-pod separation of ~5 nm. The continuous-wave photoluminescence (PL) spectra and the corresponding PL-decay curves of a bundle showed an increase of the relevant contribution of the short-pod constituent on the account of that of the long-pod partner, with variation of the their relative concentration, showing a saturation at a concentration ratio of 4:1, thus, suggesting the occurrence of a Förster resonance energy transfer (FRET) process. A mixture with equal amounts of the 11 nm and 14 nm pod-length TNCs revealed a FRET critical radius of $R_0 = 20$ nm and an optimum energy transfer rate of $10^9 s^{-1}$. The properties of this bundle were compared with a mixture of CdTe dots, comprised of radii similar to the pods' width (~4 nm) and an inter-dot spacing of ~1 nm. This comparison suggests an enhancement of an energy transfer rate among TNCs with respect to a process among adjacent dots, which may be related to the significant absorption cross-section and the large intact contact of the pods within a bundle.

1. Introduction

Colloidal semiconductor nanocrystals have attracted special attention due to the tunability of their physical properties with variation of their size. Further on, it has been found that the shape of the nanocrystals plays additional role in the control of the optical and electrical properties. For example, nanowires and nanorods exhibit enhanced conductivity and linear optical polarization along the large crystallographic axis [2]. Tetrapod nanocrystals (TNCs), composed of a central core and four pods in a tetrahedral structure, raised a special interest due to their three dimensional stretching, offering multi connections in electronic and opto-electronic circuitry [3]. While an assembly process of colloidal dots and the consequent optical properties have been investigated in recent years [4], there is nearly no knowledge on the assembly structural arrangement and the optical properties of TNCs [5].

The current work represents an assembly of CdTe TNCs, composed of two distinctive building blocks comprised of the same central core, however differed in the pod-length. The influence of the assembly arrangement, when changing the relative concentrations of the two constituents, on the optical properties was followed by monitoring the continuous-wave photoluminescence (cw-PL) and the corresponding luminescence decay processes. The results were compared with a control system,

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examining the optical property of a mixture of two batches of CdTe dots, with radii mimicking to the pods' width. The results revealed the occurrence of Förster resonance energy transfer (FRET) processes, among the constituents, with a faster energy transfer among the TNCs in comparison with the dots sample, presumably due to the significant absorption cross-section of the TNCs and the large intact contact among adjacent pods.

2. Experimental

The synthesis of the TNCs was carried out in organic media, following the procedure given in referance [3]. The shape, crystallography and size of those TNCs were determined by the use of a transmission electron microscope, T-20 Philips instrument operated at 200kV. The Raman spectra were recorded on a Jobin Yvon 23 LabRAM HR 800 UV micro-Raman spectrometer, excited at 494 nm Ar laser. The absorption spectra were recorded using JASCO-570 UV-vis spectrometer. The cw-PL spectra were recorded using a Perkin Elmer luminescence spectrometer LS 50. The PL quantum efficiency was measured with an integrating sphere Labsphere, Inc. IS-040-SL with UV-VIS-NIR reflectance coating. The PL decay curves were monitored using Nd-YAG pulse laser with exciting wavelength of 532 nm and a pulse width of 4 ns. The emitted light was focused into grating monochromator (Acton Reserch Corporations Model SpectraPro300), the signal was detected by a Hamamatsu R666 photomultiplier tube. The emission intensity was monitored at a dwell time after the laser pulse and the output was collected by a Tektronix oscilloscope model TDS 3034.

3. Results and discussion

Figure 1A represents a TEM image of a single CdTe TNC, composed of a cubic core with a tetrahedral structure and four (111) crystal facets, each facet supported the growth of a pod, with a hexagonal structure showing its (001) facets. The inset of the Figure shows a Fast Fourier Transform (FFT) picture of a single pod image, confirming the hexagonal wurtzite (WZ) structure. Figure 1B represents a TEM image of a TNCs' assemblies mixture of two kinds CdTe TNCs, both consist of 4.5 nm core, however with different pods-length of 11 nm (labeled hereon CdTe TNCs1) and 14 nm (labeled hereon CdTe TNCs2). The image suggests an inter-penetration of the pods of one kind within the territory of the other, leading to a bundle arrangement, with inter-pod spacing of \sim 5 nm.



Figure 1 (A) TEM image of a single CdTe TNC; Inset: a Fast Fourier Transform (FFT) picture of a single pod image, confirming the WZ structure. (B) TEM image of a TNCs' assemblies mixture of two kinds CdTe TNCs, both consist of 4.5 nm core, however with different pods-length of 11 nm and 14 nm.

Figuure 2A show Raman spectra of CdTe spherical dots with 4.5 nm diameter (red curve) and of CdTe TNCs1, CdTe TNCs2 (black and blue curves, respectively). All spectra exhibit a dominant resonance at 162 cm⁻¹, related to the longitudinal optics (1-LO) in zinc blende (ZB) CdTe semiconductors and its second-order replica (2-LO) at 324 cm⁻¹, with 2-LO/1-LO intensity ratio of 0.6 (Hung-Rhys factor), suggesting a relatively weak Fröhlich electron-phonon coupling in the nanocrystals at room temperature. The Raman spectra of the TNCs are distinguished by additional resonance bands, at 149 cm⁻¹, 156.5 cm⁻¹ related to surface SO mode and to a WZ 1-LO of the hexagonal pods, respectively [6]. Thus, the Raman spectra further confirm the composition of the TNCs, with a cubic ZB core and a pod with a WZ structure.



Figure 2 (A) Representative Raman spectra of CdTe spherical dots with 4.5 nm diameters (red curve) and of CdTe TNCs (see legends). (B) The absorption (dashed lines) and cw-PL spectra (solid lines) of two separate TNCs samples, according to the legend notation, measured at room temperature.

Figure 2B demonstrates the room temperature absorption (dashed lines) and cw-PL spectra (solid lines) of two separate TNCs samples (black lines = CdTe TNCs1; blue lines = CdTe TNCs2). The Figure represents a large spectral overlap between the black emission curve of CdTe TNCs1 (acceptor component) and the blue absorption curve of CdTe TNCs2 (donor component), denoted as $J(\lambda)$ by equation (1a). Also, a critical radius for an energy transfer process, denoted as R_0 , follows equation (1b) [7]:

$$J(\lambda) = \int_{0}^{\infty} f_{D}(\lambda) \varepsilon_{A}(\lambda) \lambda^{4} d\lambda$$
 (1a)

$$R_{o}^{6} = \frac{9000(\ln 10)k^{2}\phi_{D}}{128\pi^{5}n^{4}N} \int_{0}^{\infty} f_{D}(\lambda)F_{A}(\lambda)\lambda^{4}d\lambda$$
^(1b)

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 $f_D(\lambda)$ is the normalized spectrum of the donor emission, and ε_A is the acceptor extinction coefficient. ϕ_D corresponds to the PL quantum yield of the donor (~ 7%), n=2.4 is a volume weighted average refractive index (between TNCs and the surrounding), N is an Avogadro number, and k=2/3 denotes a random orientation factor between the donor and acceptor dipoles. Hence, R_0 , is estimated as 20 nm.

PL spectra of two separated CdTe TNCs1 (donor), and CdTe TNCs2 (acceptor), are shown by the red and black curves in Figure 3A.



Figure 3 (A) PL spectra of the assembly's mixture of the two CdTe TNCs1 and CdTe TNCs2 components, with different concentration ratios, Y, $(1 \le Y \le 4)$ as indicated in the legend, in comparison with the PL spectra of the pure CdTe TNCs according to the legend notation. (B) The PL decay curves of the separate donor (CdTe TNCs1) and acceptor (CdTe TNCs2), and their assemblies mixture with Y=1 detected at 660 nm and 710 nm, according to the notations given in the legend.

The cw-PL spectra of the corresponding assembly's mixture of the two CdTe TNCs1 and CdTe TNCs2 components, with different concentration ratios of CdTe TNCs2/ CdTe TNCs1, Y, as indicated in the legend of the Figure, are shown also in Figure 3A. These spectra comprised of two emission bands, showing a diminution of the donor contribution and enhancement of the acceptor emission intensity, with the increase of the acceptor/donor concentration ratio, thus suggesting a FRET process among a few donors surrounded by an increasing number of next neighbor acceptors. The PL decay curves of the separate donor and acceptor TNCs, and their mixture with Y=1 (monitored at 660 nm and at 710 nm) are shown in Figure 3B, according to the notations given in the legend. The decay processes of the separate components were fitted to a single exponent, while that of the mixtures, to a bi-exponent function (leading to an effective weighted average lifetime). The measurements reveal a quench of the donor lifetime (τ_D) and extension of the acceptor lifetime after a mix of the two sets of TNCs. The decrease in donor (CdTe TNCs1) exciton lifetime from 4.3 to 2.4 ns, accompanied by an increase in acceptor (CdTe TNCs2) exciton lifetime from 4.7 to 7.7 ns, provided evidence for enhanced FRET between the TNCs Also noting that the radiative lifetime of the donor, depends on its emission quantum yield (η), when $\tau_D = \tau_{rad} = \tau_{measured} \eta^{-1}$.

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Thus, the rate of the energy transfer between the donor and acceptor TNCs (K_{D-A}) with a mutual separation $r \sim 5$ nm is given by equation (2a), while the transfer efficiency (*E*) is defined by equation (2b):

$$K_{D-A} = \frac{1}{(\tau_D)} \left(\frac{R_0}{r}\right)^6$$
(2a)

$$E = \frac{YR_0^{\ 6}}{YR_0^{\ 6} + r^{\ 6}}$$
(2b)

Thus, the energy transfer rate between the TNCs with the 11 nm pod-length and those with the 14 nm pod-length was found to be $\sim 10^9$ s⁻¹ (for a mixture with Y=4), which is larger by an order of magnitude from that found in a mixture of dots with similar core diameters. The energy transfer rate increased from 10^8 s⁻¹ to 10^9 s⁻¹ with the increase of Y, reaching a saturation for Y=4, suggesting a complete interpenetration between pods for Y=4.

As a summary, the current work represents an assembly of CdTe TNCs, composed of two distinctive building blocks comprised of the same central core (4.5 nm in diameter), however differed in the pod-length (11 nm and 14 nm). The influence of the assembly arrangement, when changing the relative concentrations of the two constituents, on the optical properties was followed by monitoring the cw-PL and the PL-decay processes. The results were compared with a control system, examining the optical property of a mixture of two batches of CdTe dots, with radii mimicking the core diameter (or actually, the pods' width). The results revealed the occurrence of Förster resonance energy transfer processes, among the constituents, by decreasing in donor exciton lifetime from 4.3 to 2.4 ns, accompanied by an increase in acceptor exciton lifetime from 4.7 to 7.7 ns, reaching an optimum energy transfer rate of 10^9 s^{-1} among the TNCs, when complete interpenetration of the pods take place, and the feasible large intact contact of the elongated pods.

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