Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2009, **19**, 128–130

Mendeleev Communications

Growth of near-IR luminescent colloidal CdTe/CdS nanoheterostructures based on CdTe tetrapods

**Roman B. Vasiliev,*[a] Dmitry N. Dirin,[a] Maria S. Sokolikova,[a]
Sergey G. Dorofeev,[b] Alexei G. Vitukhnovsky[c] and Alexander M. Gaskov[b]**

[a] *Department of Materials Science, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 939 0998; e-mail: romvas@inorg.chem.msu.ru*
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*
[c] *P. N. Lebedev Physical Institute, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2009.05.004

Colloidal tetrapod-shaped CdTe/CdS nanoheterostructures with near-IR photoluminescence (PL) up to 830 nm were synthesized and evolution of absorption and PL spectra during shell growth was studied.

Nanometer-scale semiconductor heterostructures have attracted considerable interest in the past years due to their unique optical and electrical properties. A class of such objects is colloidal nanocrystals. Nanocrystal heterostructures demonstrate different electron and hole spatial localization after photoexcitation (type I or type II) depending on the bands offset alignments and size of semiconductor parts.[1] The most interesting one is type II for which electron and hole are confined into different parts of nanocrystal. CdTe/CdSe, CdTe/CdS, ZnSe/CdSe and CdS/ZnSe type II core/shell nanocrystals with spherical shape were previously described.[2–6] It was shown that type II systems have longer radiative decay and emit at lower energies than both core and shell semiconductors. It could have significant practical interest for development of low-threshold laser media[7] and IR biological labels for optical tomography.[8]

Moreover, modern synthetic approaches allow the preparation of branched semiconductor nanocrystals with tetrahedral symmetry – tetrapods.[9] Synthesis of anisotropic tetrapod-shaped semiconductor nanoheterostructures was pioneered by Alivisatos and co-authors.[10] Novel intriguing properties were found for such objects: giant extinction coefficients (up to 10^8 dm^3 mol^{-1} cm^{-1}),[11] polarized luminescence,[12] possibility of luminescence control by applied electric field.[13,14]

In this work, CdTe/CdS nanoheterostructures based on CdTe tetrapods were synthesized for the first time. The nanoheterostructure is composed of CdTe tetrapod with arms overcoated by CdS shell (Figure 1). Modification of optical properties during shell growth was analyzed by absorption and photoluminescent (PL) spectroscopy.

CdTe/CdS nanoheterostructures were prepared from CdTe tetrapods followed by CdS shell growth. CdTe tetrapods were synthesized according to a modified method previously reported by Peng.[15] Nanocrystal growth was carried out in diphenyl ether (Ph_2O) from cadmium oleate and tri-*n*-octylphosphine telluride (TOP:Te) under an Ar flow. Experimental details are the same as described previously.[16] Initial cadmium oleate concentration was set to [Cd] = 0.1 mol dm^{-3}, molar ratios [Cd]:[Te] = 1:1, [Cd]:[oleic acid] = 1:3, Ph_2O volume 5 ml. Tetrapod growth was carried out at 180 °C for 5 min. Finally, tetrapods were precipitated from the growth solution by acetone, washed two or three times with acetone and dissolved in hexane.

For the shell growth, an aliquote of tetrapods corresponding to about 30 mg of dried tetrapods was transferred to 5 ml of Ph_2O. The optical density of growth solution was 25 cm^{-1} at the tetrapod excitonic maximum. The number of CdTe nanoparticles was estimated from tetrapod weight with correction on about 20% weight of ligands and found to be about 10^{17}. Shell growth was carried out at 220 °C under Ar flow. Growth precursor was a mixture of 1 M tri-*n*-octylphosphine sulfide (TOP:S) solution in TOP and 0.1 M cadmium oleate solution in Ph_2O (1:1 molar ratio of [Cd]:[S]). Precursor aliquotes (0.1 mmol) were subsequently injected to the growth solution. The solution was annealed for 1 h each time before addition of next precursor portion. Overall amount of added precursor ν_{CdS} was 0.5 mmol. Colloidal solutions of CdTe/CdS nanoheterostructures in nonpolar solvents were stable for a long time.

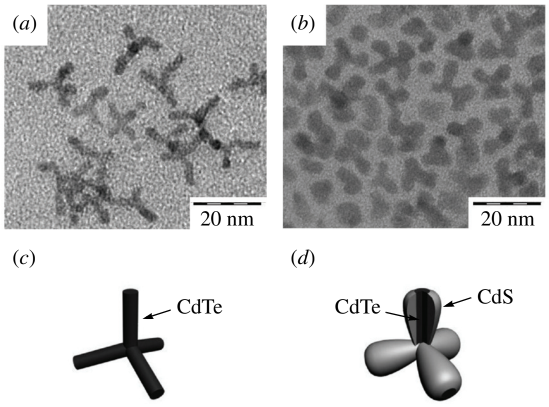

Figure 1 TEM images of (*a*) initial CdTe tetrapods and (*b*) CdTe/CdS nanoheterostructures. Schematic view of (*c*) CdTe tetrapod and (*d*) CdTe/CdS nanoheterostructure.

Nanocrystal sizes and morphology were studied by transmission electron microscopy (TEM) on a LEO912 AB OMEGA microscope. Absorption measurements were carried out on a Varian Cary50 spectrophotometer. Aliquots of 50 μl were periodically taken from growth solution and diluted with hexane up to 1 ml for absorption measurements. Wavelength λ_{abs} and absorbance A at lowest excitonic maximum were determined. All spectra were normalized to absorbance at 300 nm for the estimation of extinction coefficient of nanoparticles volume fraction.[17] Spectra were differentiated to refine of excitonic maximum position. PL measurements were carried out on a Perkin–Elmer LS55 spectrometer with excitation set to 460 nm.

Table 1 Initial tetrapod and final nanoheterostructure parameters.

Sample	d/Å	l/Å	h_{TEM}/ Å	λ_{abs}/ nm	λ_{PL}/ nm	PL FHWM/ nm	QY (%)
CdTe	22±3	90±7	—	620	640	47	<1
CdTe/CdS	46±7	90±6	12	720[a]	830	107	24

[a] From second derivative of absorption spectrum.

Quantum yields (QY) were determined relative to Rhodamine 6G dye (ethanol solution with optical density ~0.1 at excitation wavelength, 95% QY).

The TEM image of CdTe tetrapods is shown in Figure 1(*a*). Average diameter of tetrapod arms is $d = 2.2$ nm, and average arm length is $l = 9$ nm. After shell growth [Figure 1(*b*)], tetrapod arms became thicker, but their length remained invariable. This allows one to estimate average shell thickness h_{TEM} as 1.0–1.4 nm that corresponds to about three monolayers of CdS. Parameters of tetrapods and nanoheterostructures are listed in Table 1. Note that a fraction of spherical particles was observed. We suppose that may result from CdS shell growth on CdTe nanorods, which were found as an impurity for initial CdTe tetrapods. No parallel CdS nanoparticles formation was detected that confirmed by optical measurements as absence of CdS excitonic maximum in blue region.

Absorption spectrum of initial CdTe tetrapods has a distinctive excitonic peak at 620 nm with FWHM of about 20 nm. Quantum yield of tetrapods was less than 1% with PL maximum λ_{PL} at 640 nm. Changes of CdTe/CdS absorption and PL spectra during the shell growth are shown in Figure 2. Shell growth leads to a monotonic shift of λ_{abs} to a longer wavelength. At the same time, absorbance at excitonic maximum decreases and the distinctive peak in the absorption spectrum of the initial core is replaced by a nearly featureless absorption tail typical of spherical type II nanocrystals.[2] At the same time λ_{PL} shifted into near-IR region by 0.4 eV relative to initial tetrapods. PL maximum of final CdTe/CdS nanoheterostructures lies near 830 nm and their QY is approximately 20%. It should be noted that luminescence for previously described tetrapod-based CdTe/CdSe nanoheterostructures was not observed[18] due to high spatial separation of electron and hole, as the authors suppose.

Kinetics of λ_{abs} variation after 0.1 mmol precursor addition is shown in insert in Figure 3(*a*). Shift rate became slower in time as a result of precursor depletion. Saturation time for λ_{abs} shift was about 60 min. This period should correspond to complete precursor deposition. Thus, shell thickness h_{theor} may be estimated for each added aliquot. Calculated thickness of the final sample is in well agreement with h_{TEM}.

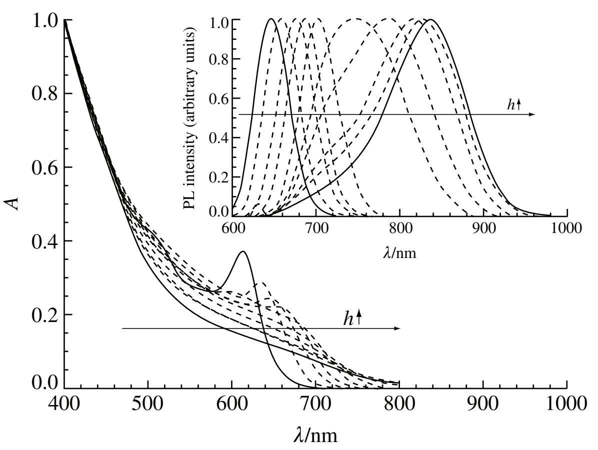

Figure 2 Evolution of absorption and luminescence (insert) spectra of CdTe/CdS sample during CdS shell growth. Solid lines, initial and final samples; dashed lines, probes.

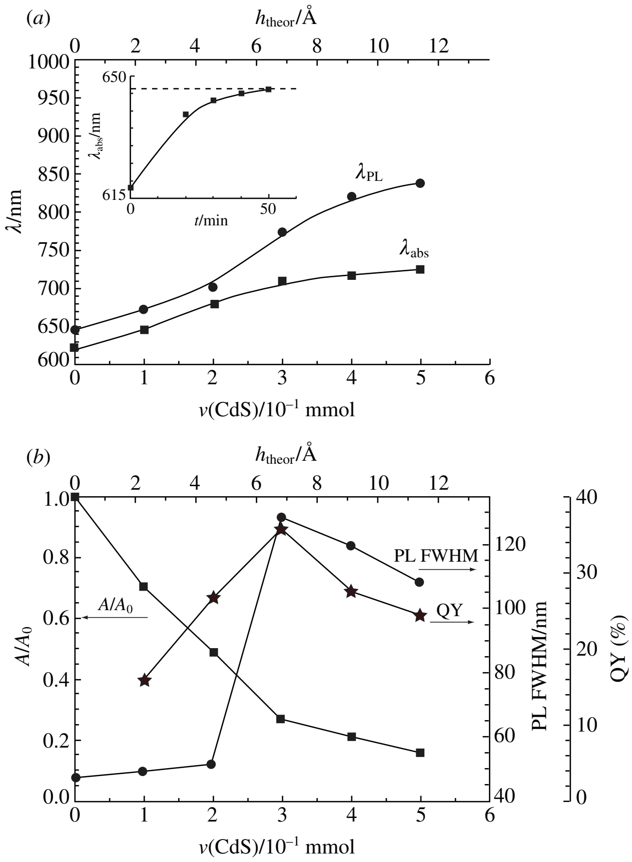

Figure 3 (*a*) Shell growth dependence of absorption λ_{abs} and photoluminescence λ_{PL} maxima and (*b*) normalized absorbance A/A_0, QY and PL FWHM of CdTe/CdS sample. Insert: kinetics of λ_{abs} variation after addition of 0.1 mmol of precursors.

Dependence of λ_{abs} and λ_{PL} as a function of h_{theor} is shown in Figure 3(*a*) for each precursor aliquot. Significant discrepancy between λ_{abs} and λ_{PL} (global Stocks shift) was found for shell thickness > 0.5 nm. Stocks shift for the final nanoheterostructures was about 110 nm. This is considerably greater than Stocks shift of initial tetrapods (20 nm). Such a behavior may be a result of PL emitting level change due to electron-hole symmetry switching, as described for CdTe tetrapods.[19] For initial tetrapods, electron is mostly confined in zinc blende core, whereas the hole is located in arms. Shell thickness increase leads to localization of electron into the shell, *i.e.*, in arms. PL FWHM increase [Figure 3(*b*)] also confirms our suggestion of emitting level change.

Ten times diminution of absorbance at excitonic band was observed during the shell growth [Figure 3(*b*)]. For clearness, the value of A was normalized to absorbance A_0 of initial tetrapods. Quantum yield jumps up to 35% at the beginning of the shell growth due to the surface traps passivation. Subsequent shell growth leads to QY decrease. It is in agreement with small overlap of electron and hole wave functions, which leads to an increase in the probability of nonradiative relaxation. Both near-IR luminescence shift and significant decrease of excitonic absorption may indicate the formation of type II separation regime for synthesized CdTe/CdS nanoheterostructures.

In conclusion, colloidal CdTe/CdS nanoheterostructures with near-IR photoluminescence up to 830 nm and 20% quantum yield were synthesized on the basis of CdTe tetrapods. Evolution of absorption and PL spectra during CdS shell growth was analyzed. It was shown that increase of shell thickness leads to decrease in excitonic absorbance till the featureless tail formation. At the same time, PL maximum shifts to IR region by about 0.4 eV relative to initial CdTe tetrapods. These facts may indicate the formation of type II separation regime. Observed PL FWHM and Stocks shift increase may point to the change of PL optical transition.

This work was supported by the Russian Foundation for Basic Research (grant no. 07-03-00843) and the President of the Russian Federation (grant no. MK-5074.2007.3). The TEM investigations were carried out at the Center of Electron Microscopy, Moscow State University.

References

1 A. Piryatinski, S. A. Ivanov, S. Tretiak and V. I. Klimov, *Nano Lett.*, 2007, **7**, 108.

2 S. Kim, B. Fisher, H.-J. Eisler and M. Bawendi, *J. Am. Chem. Soc.*, 2003, **125**, 11466.

3 J. J. Li, J. M. Tsay, X. Michalet and S. Weiss, *Chem. Phys.*, 2005, **318**, 82.

4 O. Schops, N. Le Thomas, U. Woggon and M. V. Artemyev, *J. Phys. Chem. B*, 2006, **110**, 2074.

5 L. P. Balet, S. A. Ivanov, A. Piryatinski, M. Achermann and V. I. Klimov, *Nano Lett.*, 2004, **4**, 1485.

6 S. A. Ivanov, A. Piryatinski, J. Nanda, S. Tretiak, K. R. Zavadil, W. O. Wallace, D. Werder and V. I. Klimov, *J. Am. Chem. Soc.*, 2007, **129**, 11708.

7 V. I. Klimov, S. A. Ivanov, J. Nanda, M. Achermann, I. Bezel, J. A. McGuire and A. Piryatinski, *Nature*, 2007, **447**, 441.

8 S. Kim, Y. T. Lim, E. G. Soltesz, A. M .De Grand, J. Lee, A. Nakayama, J. A. Parker, T. Mihaljevic, R. G. Laurence, D. M. Dor, L. H. Cohn, M. G. Bawendi and J. V. Frangioni, *Nat. Biotechnol.*, 2004, **22**, 93.

9 L. Manna, D. J. Milliron, A. Meisel, E. C. Scher and A. P. Alivisatos, *Nat. Mater.*, 2003, **2**, 382.

10 D. J. Milliron, S. M. Hughes, Y. Cui, L. Manna, J. Li, L.-W. Wang and A. P. Alivisatos, *Nature*, 2004, **430**, 190.

11 D. V. Talapin, J. H. Nelson, E. V. Shevchenko, S. Aloni, B. Sadtler and A. P. Alivisatos, *Nano Lett.*, 2007, **7**, 2951.

12 C. Mauser, T. Limmer, E. Da Como, K. Becker, A. L. Rogach, J. Feldmann and D. V. Talapin, *Phys. Rev. B*, 2008, **77**, 153303.

13 K. Becker, J. M. Lupton, J. Müller, A. L. Rogach, D. V. Talapin, H. Weller and J. Feldmann, *Nat. Mater.*, 2006, **5**, 777.

14 R. M. Kraus, P. G. Lagoudakis, A. L. Rogach, D. V. Talapin, H. Weller, J. M. Lupton and J. Feldmann, *Phys. Rev. Lett.*, 2007, **98**, 017401.

15 W. W. Yu, Y. A. Wang and X. Peng, *Chem. Mater.*, 2003, **15**, 4300.

16 R. B. Vasiliev, S. G. Dorofeev, D. N. Dirin, D. A. Belov and T. A. Kuznetsova, *Mendeleev Commun.*, 2004, 169.

17 V. I. Klimov, *J. Phys. Chem. B*, 2000, **104**, 6112.

18 P. Peng, D. J. Milliron, S. M. Hughes, J. C. Johnson, A. P. Alivisatos and R. J. Saykally, *Nano Lett.*, 2005, **5**, 1809.

19 D. Tarì, M. De Giorgi, F. D. Sala, L. Carbone, R. Krahne, L. Manna, R. Cingolani, S. Kudera and W. J. Parak, *Appl. Phys. Lett.*, 2005, **87**, 224101.

Received: 14th November 2008; Com. 08/3237