

Time-Resolved Laser Spectroscopy of Highly Photoluminescent Silica-Coated CdTe Nanocrystals

Gabriel Sagarzazu¹, Yoichi Kobayashi¹, Norio Murase², Ping Yang² and Naoto Tamai¹

¹*School of Science and Technology, Kwansai Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337 Japan*

²*Health Research Institute, National Institute of Advanced Industrial Science and Technology, Midorigaoka, Ikeda-city, Osaka 563-8577 Japan*

Semiconductor quantum dots (QDs) have received wide interest over the past decades, especially thanks to their size-dependent emission, their good photoluminescence efficiency and their superior photostability as compared to that of conventional organic fluorophores. The unique photophysical properties of these nanoparticles justify their increasing use in biophotonic applications for highly sensitive detection. In the view of providing water solubility, chemical robustness and biocompatibility, which are major requirements for bio-applications, a typical strategy consists in coating these nanocrystals (NCs) with SiO₂. Nevertheless, it has been observed that such coatings usually lead to a decrease of the photoluminescence (PL) efficiency of the QDs.

Recently, Murase and Yang observed that CdTe NCs coated with a SiO₂ shell containing small CdS-like clusters (see Figure 1) show enhanced photoluminescence [1]. These hybrid NCs were synthesized from colloiddally prepared CdTe NCs coated with a thin SiO₂ layer by sol-gel techniques. After the reflux step, which corresponds to the CdS-like clusters formation in the silica layer, a red-shift of the absorption and emission spectra accompanied by spectral narrowing is observed. The promising spectroscopic properties obtained from this new type of surface passivation may partly originate from the fact that the CdS-like clusters are not bound to the surface of the CdTe NCs. Therefore, a lattice constant mismatch and lattice defects in the shell due to distortion have no effect.

From these observations, time-resolved experiments have been performed in order to gain a better understanding of the photophysical mechanisms of these highly luminescent particles. Several samples have been analyzed, which correspond to different reflux conditions, i.e. to different sizes of the CdS-like clusters, and thus, to different peak positions of the absorption and PL peaks.

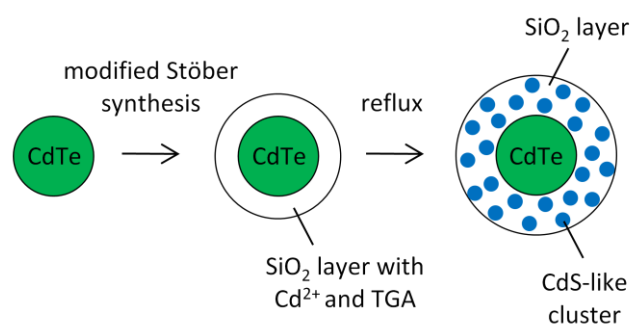


Figure 1. Model of the synthesis of hybrid SiO₂-coated CdTe nanocrystals. After reflux, small CdS-like clusters (~1nm or less) are present in the silica layer.

The luminescence decays of hybrid SiO₂-coated CdTe NCs can be fitted with a bi-exponential function whose fast component is attributed to the exciton recombination while the slow component may originate from the surface-related emission of the NCs [2,3]. This analysis shows an increase of the intensity average lifetime with the size of the clusters. The variations of the fluorescence decay is comparable to that observed in studies on type II CdTe/CdS or CdTe/CdSe core/shell NCs [3,4]. We thus believe that the probability function of electrons may extend outside the CdTe cores in the presence of CdS-like clusters. This interpretation also justifies the spectral red-shift with the formation of the clusters corresponding to a lower quantum confinement in the NC.

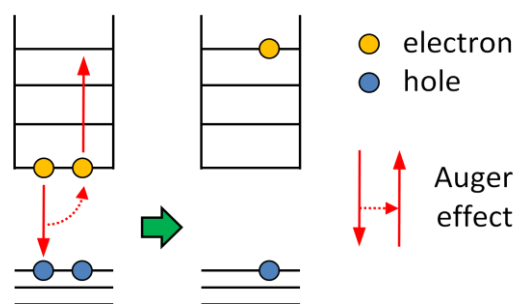


Figure 2. Schematic of biexciton Auger recombination. The non-radiative recombination energy of an electron-hole pair is transferred to a third carrier.

Subsequently, we examined the effect of the CdS-like clusters on biexciton Auger recombination. As represented in Figure 2, biexciton Auger recombination is a three-particle process where the energy of an electron-hole recombination is non-radiatively transferred to a third carrier (electron or hole). Even though Auger processes, which are mediated by Coulomb electron-electron interactions, are greatly reduced in bulk semiconductors, its efficiency dramatically increase in QDs. Auger effect is known to be responsible of autoionization of semiconductor NCs, inducing luminescence intermittency (blinking) in single-NC studies. For an assembly of fluorophores,

Auger auto-ionization directly results in a decrease of the total luminescence intensity. We examined the carrier population dynamics by femtosecond transient spectroscopy. At low excitation intensities, the dynamics of biexciton Auger recombination closely follows a bi-exponential law. The slow component of the fitting function corresponds to the linear relaxation rate while the biexciton recombination is observable at short time scales ($\Delta t \approx 10$ ps).

Transient absorption spectra of SiO₂-coated CdTe NCs were examined as a function of the intensity. For each sample, a global analysis of several datasets corresponding to low excitation intensities shows an increase of the Auger recombination lifetime with the size of the CdS-like clusters. Such conclusion is in good agreement with the results obtained from the fluorescence decay experiments. While the lengthening of the intensity average lifetime may be caused by an extension of the probability function of electrons outside the CdTe cores, the presence of CdS-like clusters also results in less efficient Auger processes in the QDs, reducing the blinking behavior of these particles and enhancing their fluorescence at a macroscopic scale. Such a conclusion may be an important interpretation of the improvement of the PL efficiency observed in hybrid SiO₂-coated CdTe nanocrystals.

References

- [1] N. Murase, P. Yang, *Small* **2009**, 5, 800-803.
- [2] P. Yang, N. Murase, *Adv. Funct. Mater.* **2010**, 20, 1258-1265.
- [3] Q. Zeng, X. Kong, Y. Sun, Y. Zhang, L. Tu, J. Zhao, H. Zhang, *J. Phys. Chem. C* **2008**, 112, 8587-8593.
- [4] P. T. K. Chin, C. M. de Donega, S. S. van Bavel, S. C. J. Meskers, N. A. J. M. Sommerdijk, R. A. J. Janssen, *J. Am. Chem. Soc.* **2007**, 129, 14880-14886.