

## Effect of electric field on CdSe/CdS/ZnS nanocrystals

Sreeparvathi Warriar<sup>1</sup>, Karel Lambert<sup>2</sup>, Jolien Dendooven<sup>3</sup>, Christophe Detavernier<sup>3</sup>, Zeger Hens<sup>2</sup>, Dries Van Thourhout<sup>1</sup>

<sup>1</sup> Photonics Research Group, INTEC-department, Ghent University - IMEC, Sint-Pietersnieuwstraat 41, 9000 Gent, Belgium

<sup>2</sup> Physics and Chemistry of Nanostructures, Department of Physical and Inorganic Chemistry, Ghent University, Krijgslaan 281-S3, Gent, Belgium

<sup>3</sup> Coating and Contacting of Nanostructures, Department of Solid State Sciences, Ghent University, Krijgslaan 281-S1, Gent, Belgium

*The influence of the stark effect on the fluorescence spectrum of CdSe/CdS/ZnS heterogeneous quantum dots with bandgap in the visible region has been studied. A nanocrystal monolayer was sandwiched between Al<sub>2</sub>O<sub>3</sub> and ITO layers. Fields from 10<sup>-5</sup> V/cm to 10x10<sup>-5</sup> V/cm were applied. A decrease in luminescence peak amplitude of almost 85% and a red shift in peak energy of 35meV have been observed for the highest applied field. The shift is reversible and can be fit to a second order polynomial. This suggests the applicability of these materials for electro-optic modulation devices.*

### Introduction

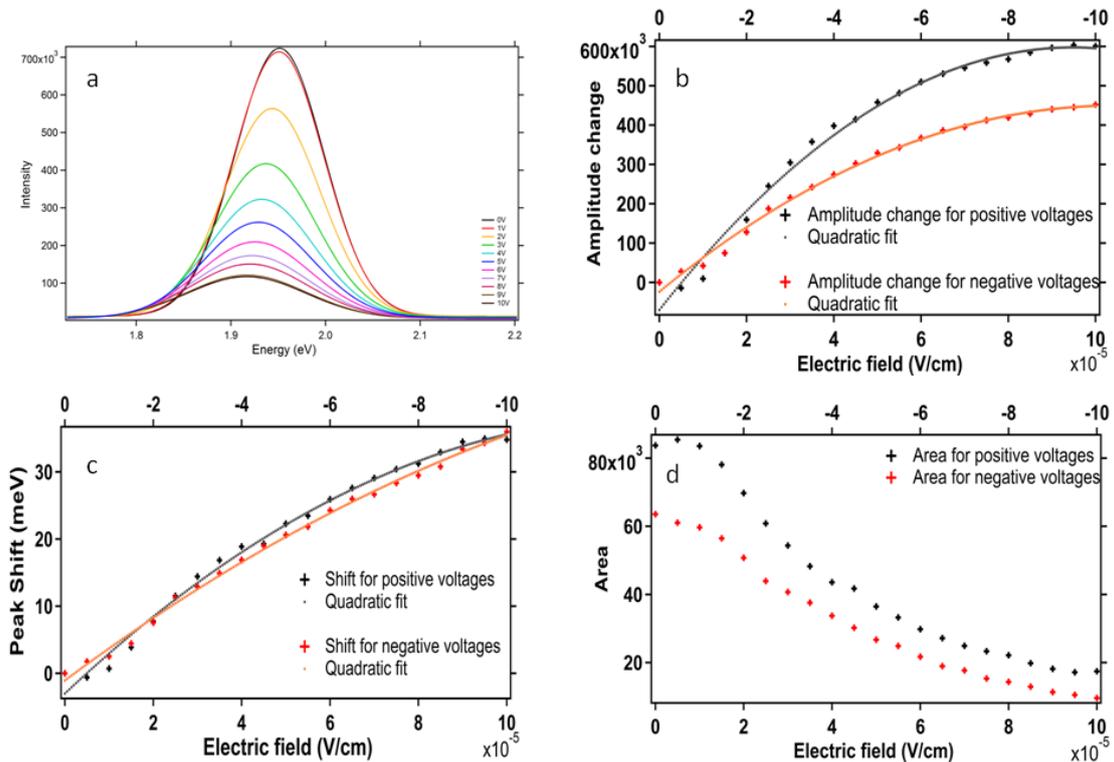
Quantum dots, the zero dimensional analog of quantum wells, represent the ultimate in semiconductor based quantum confined systems. The optical and electronic properties in quantum confined systems are tunable with the size of the confinement dimension and hence quantum confined systems provide the opportunity to tailor the optical properties to the needs of an application. The change in property at this length scale in semiconductors is due to further confinement of the electronic motion to a length scale that is comparable to or smaller than the exciton Bohr radius. Also these systems possess large oscillator strength and polarizabilities relative to bulk and hence are good candidates for electro-optic and non-linear devices. [1] In the past couple of decades there has been an exponential growth in activities in this field, driven both by excitement of understanding new science and by the potential hope for applications and economic impacts. [1] Colloidal quantum dots are a class of nanomaterials synthesized from organic solutions. They are easy to prepare when compared to the top down approach involving lithography. Narrow transition linewidths inherent in dots coupled with large stark shifts, should result in electro-optic modulation devices with high efficiency. Size tunable properties of CdSe in the visible spectrum has attracted lot of attention. Much experimental work has been done to improve stability and luminescence efficiency. To suppress the surface effects, inorganic passivation with wide bandgap material is a well developed solution.[4, 5] The CdSe/CdS core/shell nanocrystal has less lattice mismatch (3.9%) between the core and shell than the CdSe/ZnS nanocrystal (12%), so it can provide better stability by decreasing interfacial strain. However, the energy levels of the valence band maximum and conduction band minimum of CdS are not enough to confine both electrons and holes in the CdSe core so that the CdSe/CdS nanostructure exhibited less quantum yield compared to CdSe/ZnS.[6] In order to solve above limitation the core multishell structures such as CdSe/CdS/ZnS have been

prepared by inserting an interlayer between the CdSe core and ZnS outershell.[7]

## Sample preparation and measurement

CdSe core synthesis is based on a procedure described by Jasieniak et al.[8, 9] Subsequent CdS and ZnS shells were grown using a slightly modified version of the Successive Ionic Layer Adsorption and Reaction (SILAR) procedure reported by Xie et al.[10] The final diameter of the nanocrystals were 8.17nm. A nanocrystal monolayer was sandwiched between Al<sub>2</sub>O<sub>3</sub> (50 nm) and ITO. Commercially available ITO coated glass served as the bottom contact while the top ITO was deposited by vapor deposition technique. Al<sub>2</sub>O<sub>3</sub> was deposited by Atomic Layer Deposition technique and the Langmuir Blodgett method was used to make nanocrystal monolayer. Fluorescence microscopy was used to study the quantum confined stark effect. The samples were kept at room temperature and excited at 400nm. Excitation beam was incident perpendicularly to the sample and hence parallel to the direction of applied field. A series of emission spectra were taken at different applied voltages ranging from 0 to 10V.

## Result



The change in fluorescence peak position and amplitude with applied field can be seen in figure *a* and *b*. We see a slight red shift and a decrease in peak amplitude with increasing field. A field of  $10 \times 10^{-5}$  V/cm produces a peak shift equivalent to 35 meV and a decrease in peak amplitude of almost 85% (figure *b*). The shift is reversible though not exactly reproducible. A plot of stark shift as a function of field can be fit to a quadratic

function of field indicating the presence of polarizable character in emitting state. There is also an increase in fluorescence linewidth with increase in applied field.

## References

- [1] Sacra A. Stark Spectroscopy of CdSe Nanocrystallites. 1996.
- [2] Burda C, Chen X, Narayanan R, El-sayed MA. "Chemistry and Properties of Nanocrystals of Different Shapes," *Chem. Rev.* 105, 1025-1102, 2005
- [3] Empedocles S.A, Bawendi M.G, "Quantum confined stark effect in single CdSe nanocrystallite quantum dots," *Science*. 278, 2114, 1997
- [4] L. Xu, L. Wang, X. Huang, J. Zhu, H. Chen, K. Chen, "Surface passivation and enhanced quantum-size effect and photo stability of coated CdSe/CdS nanocrystals," *Physica E* 8, 129–133, 2000
- [5] J. Li, Y.A. Wang, W. Guo, J.C. Keay, T.D. Mishima, M.B. Johnson, and X. Peng, "Large-scale synthesis of nearly monodisperse CdSe/CdS core/shell nanocrystals using air-stable reagents via successive ion layer adsorption and reaction, *J. Am. Chem. Soc.* 125,12567–12575, 2003
- [6] S. Jun, E. Jang, and J.E. Lim, "Synthesis of multi-shell nanocrystals by a single step coating process," *Nanotechnology*. 17, 3892–3896, 2006
- [7] D.V. Talapin, I. Mekis, S. Go" etzinger, A. Kornowski, O. Benson, and H. Weller, "CdSe/CdS/ ZnS and CdSe/ZnSe/ZnS core-shell-shell nanocrystals," *J. Phys. Chem. B*. 108, 18826–18831, 2004
- [8] J. Jasieniak, C. Bullen, J. Van Embden, P. Mulvaney,"Phosphine free synthesis of CdSe nanocrystals" *J. Phys. Chem. B*. 109, 20665, 2005
- [9] K. Lambert, R. K. Capek, M. I. Bodnarchuk, M. V. Kovalenko, D. Van Thourhout, W. Heiss, Z. Hens," Langmuir-Schaefer deposition of quantum dot multilayers." *Langmuir*. 26, 7732, 2010
- [10] R. Xie, U. Kolb, J. Li, T. Basché, A. Mews, "Synthesis and Characterization of Highly Luminescent CdSe–Core CdS/Zn<sub>0.5</sub>Cd<sub>0.5</sub>S/ZnS Multishell Nanocrystals," *J. Am. Chem. Soc.* 127, 7480, 2005

The research leading to these results has received funding from the European Community's Seventh Framework Programme under grant agreement no.214954.

