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TEM Characterization and Optical Properties of Hetero-Structured ZnO/CdS Quantum Dots with Long Exciton Lifetime

V.V. Volkov[1], Y. Zhu[1], I.L. Kuskovski[2], V.A. Shuvayev[2], F. Xu[3], H. Matsui[3]
[1] CMPMS Department, Brookhaven National Laboratory, Upton, NY 11973
[2] Dept. of Physics, City University of New York, Queens College, Flushing, New York 11367
[3] Dept. of Chemistry and Biochemistry, City University of New York, Hunter College, NY 10065

The tunability of electronic and optical properties of semiconductor nano-crystalline quantum dots (QDs) has been an important subject in nanotechnology. While the control of emission properties of QDs on different wavelengths has been studied extensively, the control of emission lifetimes for many types of QDs has not been explored in depth. In this work we provide combined TEM/ED/EDX characterization in parallel with optical properties measurement for the new ZnO-CdS member from family of AII-BVI hetero-structured QDs, especially important for visible optical range and solar applications. Such novel QDs were synthesized in two-step process [1], starting with synthesis of core ZnO nanoparticles followed by the slow stepwise growth of CdS shells. The energy-band diagram ZnO-CdS (Fig.1a) is specific for type-II heterostructures and favors effective electron-hole spatial separation at hetero-junction interfaces ZnO-CdS upon QDs photon's excitation, potentially leading to long-living excitons and long photoluminescence (PL) decay times.

As mentioned above, type-II ZnO-CdS QDs were examined by several TEM methods, including BF/DF-contrast, HREM lattice imaging and Fourier-diffraction analysis for single QD's, nanoarea ED patterns and nanoarea-acquired EDX-spectra used for nano-phase identification, microstructure and composition analysis down to single ZnO-CdS nanoparticles of averaged size ~5-6 nm (Fig.1). Our TEM observations for colloidal ZnO-CdS QDs have been correlated with their chemical composition, growth parameters and optical properties measurements, including UV/Vis absorption-photoluminescence spectra and time-resolved photoluminescence (PL) by direct PL-decay time measurements in nanosecond-time domain (Fig.2). Experimental results are compared with quantum-mechanic band structure predictions by taking into account quantum-confinement effects.
In brief, our observations suggest that ZnO-CdS QDs crystallize in common hexagonal structure with lattice parameters close to bulk hexagonal CdS. Analysis of TEM/ED/HREM/EDX-data shows that at nanoscale QDs behave as single-phase material, suggesting reaction mechanism controlled by the homomorphic epitaxial intergrowth for hetero-structured QDs. However, their variable ZnO/CdS composition is sensitive to total growth-reaction time of CdS-shell, leading to larger particle size, CdS-rich composition shift, and observed red-shifts in optical spectra versus particle shell size.

Finally, coating of CdS shell on a ZnO core creates the new type-II QDs with strongly-enhanced exciton life-time. Indeed, for these QDs our measured PL-decay time (Fig.2) has increased more then 100 times (~100-200 ns) in contrast to pure core-ZnO QDs (~1ns), and the lifetime was further extended as the thickness of shell increased. These results are of scientific and practical importance. Since ZnO-CdS QDs operate in visible optical range, they can be used for improved photoluminescent markers, in medical imaging, photonics, solar cells, nanoelectronics, and biosensors.

[1] F. Xu, V.V. Volkov, Y. Zhu, H. Bai, A. Rea, N.V. Valappil, X. Gao, I.L. Kuskovsky, and H. Matsui, *J. Phys. Chem. C* , **113** (45), 19419-19423 (2009).
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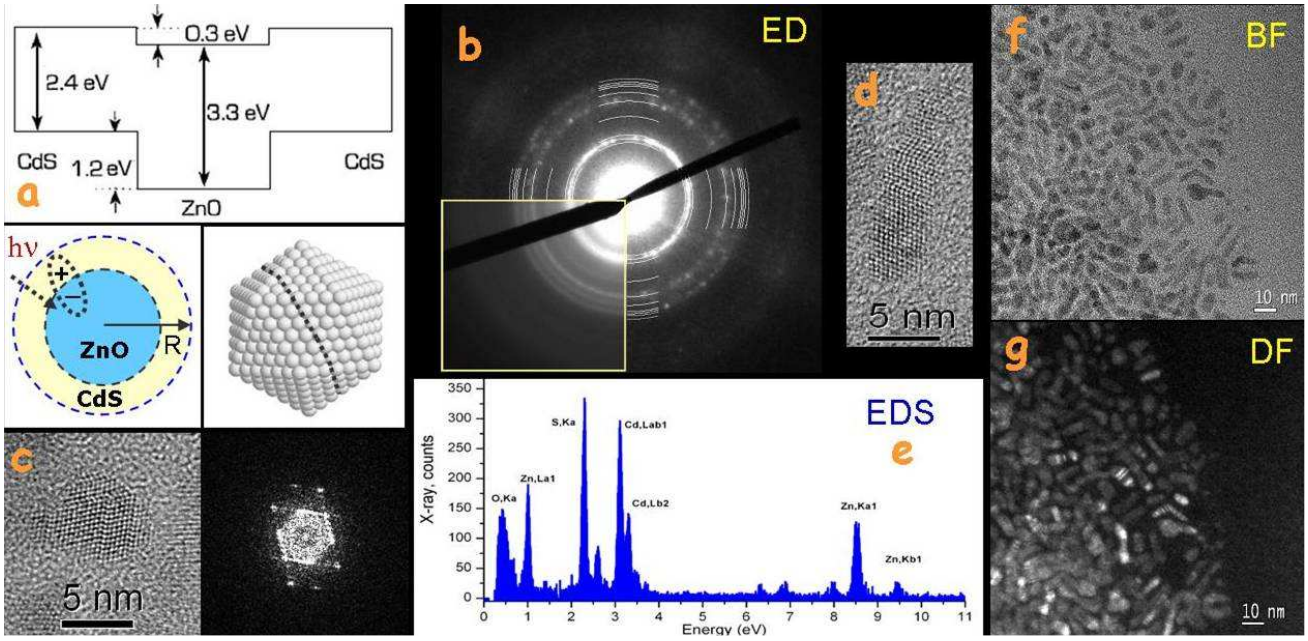

Fig.1. (a) Band Structure and schematic structure for type-II ZnO-CdS QDs in core-shell geometry. (b) SAED pattern of ZnO/CdS QDs compared to reference CdS NPs (yellow inset). (c,d) HREM images of some selected nanoparticles. (e) Typical nano-area EDS-spectrum from single or group of 2-3 nanoparticles. (f,g) Complementary bright/dark-field images of QDs illustrating effects of crystal twinning at nanoscale.

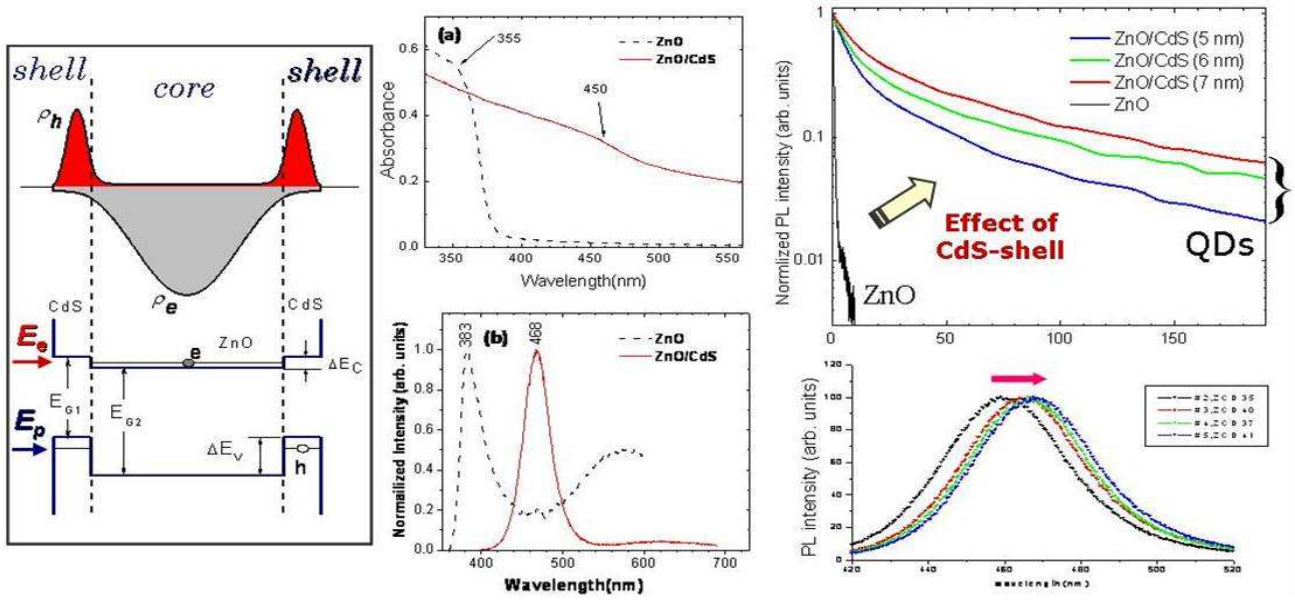

Fig.2. Effect of quantum confinement and electron-hole charge separation in QDs ZnO-CdS (left). Absorbance (a) and PL (b) spectra (middle column). Time-resolved PL decay (nsec) spectra for ZnO/CdS QDs vs. ZnO and effect of red shift (red arrow) in PL-spectra versus growing QDs particle size (from #2 to #5) (right column).

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