

## Internal Atomic-Scale Structure, Band Alignment and Charge Transfer Dynamics of ZnTe/CdSe Core/Shell Quantum Dots

Cecilia M. Gentle(1), Tyler Haddock(1), Conner Dykstra(1), Gilles Doumy(2), Anne Marie March(2), Renske M. van der Veen(1)

(1) Department of Chemistry, University of Illinois at Urbana-Champaign, USA

(2) Chemical Sciences and Engineering Division, Argonne National Laboratory, Illinois, USA  
[gentle2@illinois.edu](mailto:gentle2@illinois.edu)

**Introduction:** Heterostructured nanomaterials (i.e. core/shell quantum dots, quantum dot-metal oxides, heterostructured rods) are ideal high efficiency solar energy chromophores because of the broad absorption spectra, excellent photostability of quantum dots, as well as their promising potential to increase the conversion efficiency above the Shockley-Queisser limit. The aim of this project is to unravel the internal atomic-scale structure, band alignment and charge transfer dynamics of Type II ZnTe/CdSe core/shell quantum dots (CSQDs). To achieve this goal, a multitude of static and ultrafast characterization tools, including femtosecond-resolved laser spectroscopy and picosecond resolved X-ray absorption spectroscopy are used.

**Methods:** ZnTe/CdSe CSQDs were synthesized as described in the literature. EXAFS measurements in partial fluorescence mode were done at the 9BM and 20BM beam lines at the APS at Argonne National Lab. Time-resolved-XAS measurements were performed at the 7ID-D beam line at the APS. Samples were circulated using a fast-flowing Microliquids GmbH jet in order to refresh the sample between laser shots. Signal collection was done in total fluorescence mode with two APD detectors. The experiments were performed during the 24 bunch electron filling pattern at the APS. The laser used for sample excitation was a Pharos laser at its second harmonic (515 nm) with a 931 kHz repetition rate and  $\sim 750$  fs pulses. While the sample was excited with fs laser pulses, the overall  $\sim 70$  ps time resolution is determined by the X-ray pulse length. Difference ('on'-'off') spectra are generated on a pulse-by-pulse basis in order to eliminate systematic errors due to drifts.

**Results and discussion:** Our static EXAFS results at the Zn and Se K-edges confirm the presence of pure zinc blende (ZB) ZnTe and CdSe phases in the core-shell quantum dots. On the other hand, EXAFS at the Cd and Te K-edges indicate the presence of an intermediate CdTe layer at the core-shell interface. Such interface layer was suggested in the literature, but unambiguous element-specific analysis was lacking so far. Initial ps-resolved XAS results show clear transient features at both the Se and Zn K-edges. When compared to a static difference spectrum, it is evident that the transient cannot be explained by a simple shift of the ionization edge. A first qualitative analysis indicates contributions from photoinduced charge transfer and band filling/depletion to the transient XANES spectrum, as well as structural rearrangements affecting the higher-energy transient XANES/EXAFS spectra. We are currently performing FEFF calculations to disentangle the various processes and obtain a more quantitative picture of charge transfer dynamics. Laser induced heating of the sample may contribute to the apparent red shift observed at both edges. For the laser fluences employed we expect temperature increases of the nanoparticle between on the order of  $\sim 100$ -300 K. Heat diffusion calculations are underway to estimate the nanoparticle cooling times. Heat controlled static XAS experiments will be conducted to estimate the magnitude of this effect.

**Conclusion(s):** Further ultrafast XAS studies on the Cd and Te edges and fs optical transient absorption studies will provide a full picture of the charge separated state in ZnTe/CdSe CSQDs.

**Support Acknowledgment:** This material is based upon work supported by the Robert C. and Carolyn J. Springborn Endowment for Student Support Program and the National Science Foundation Graduate Research Fellowship Program. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation. This research was carried out in part in the Frederick Seitz Materials Research Laboratory Central Research Facilities, University of Illinois. Additionally, this research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.