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Quantification of Material Gradients in Nanocrystals

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Core/shell nanocrystals in which the materials change gradually from core to shell are very very promising structures to optimise the opto-electronic properties and quantum efficiencies of nanoscale semiconductors. Gradients are able to minimise crystal defects, lattice mismatch, and can be used to engineer the envelope wave function of excitons in order to suppress non-radiative Auger processes. However, due to the small size of the particles, so far no reliable method exists to quantify the extent of such a gradient.

In this work we have measured the material gradient of ZnSe/CdS core/shell nanocrystals, which were synthesised at elevated temperatures (260 and 290 ℃), which controls the rate of radial ion migration. We used EXAFS spectroscopy to determine the average coordination of selenium ions, which were fitted to a continuum model for the radial distribution of cations and anions [2].

It could be shown that for the 260 ℃ sample the data shows strong cation migration, which transports significant amounts (> 50%) of cadmium into the core, while the anion gradient is consistent with negligible ion migration beyond the interfacial monolayer. This is significant, because many shell growth protocols that are assumed to produce sharp interfaces are performed at similar temperatures. At higher temperatures of 290 ℃ the data deviates strongly from the model, with effectively less cation migration. This is explained by the formation of an ordered Zn0.5Cd0.5Se superlattice in the core in order to mitigate the lattice mismatch die to the increasing CdSe content of the core [3]. Raman spectroscopy shows selective resonant enhancement of the core LO phonon overtones, which indicates that the exciton is primarily localized in the core and at interfacial traps, and that the electronic structure flips from a type-II to a type-I system.

Hence, the combination of X-ray and Raman spectroscopy is able to identify both the chemical and electronic structure of core/shell particles and produces an accurate gradient model that can be employed in more precise and predictive structural calculations. The high-temperature product sheds light on why some highly emissive nanocrystals still blink and struggle to reach unity quantum yield [4].

References:
[1] Boldt, K.; Bartlett, S.; Kirkwood, N.; Johannessen, B. Quantification of Material Gradients in Core/Shell Nanocrystals Using EXAFS Spectroscopy. Nano Lett. 2020, 20, 1009-1017.
[2] Cragg, G. E.; Efros, A. L. Suppression of Auger Processes in Confined Structures. Nano Lett. 2010, 10, 313-317.
[3] Wei, S. H.; Ferreira, L. G.; Zunger, A. First-Principlescalculation of Temperature-Composition Phase of Semiconductor Alloys. Phys. Rev. B 1990, 41, 8240-8269.
[4] Boldt, K.; Kirkwood, N.; Beane, G. A.; Mulvaney, P. Synthesis of Highly Luminescent and Photo-Stable, Graded Shell CdSe/CdxZn1-xS Nanoparticles by In Situ Alloying. Chem. Mater. 2013, 25, 4731-4738.

Primary author(s) : Dr KLAUS, Boldt (University of Konstanz)

Co-author(s) : Dr BARTLETT, Stuart (Diamond Light Source); Dr KIRKWOOD, Nicholas (The University of Melbourne); JOHANNESSEN, Bernt (Australian Synchrotron)

Presenter(s) : Dr KLAUS, Boldt (University of Konstanz)

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