Unravelling the internal structure of complex nanocrystals: Spectroscopy beyond Microscopy

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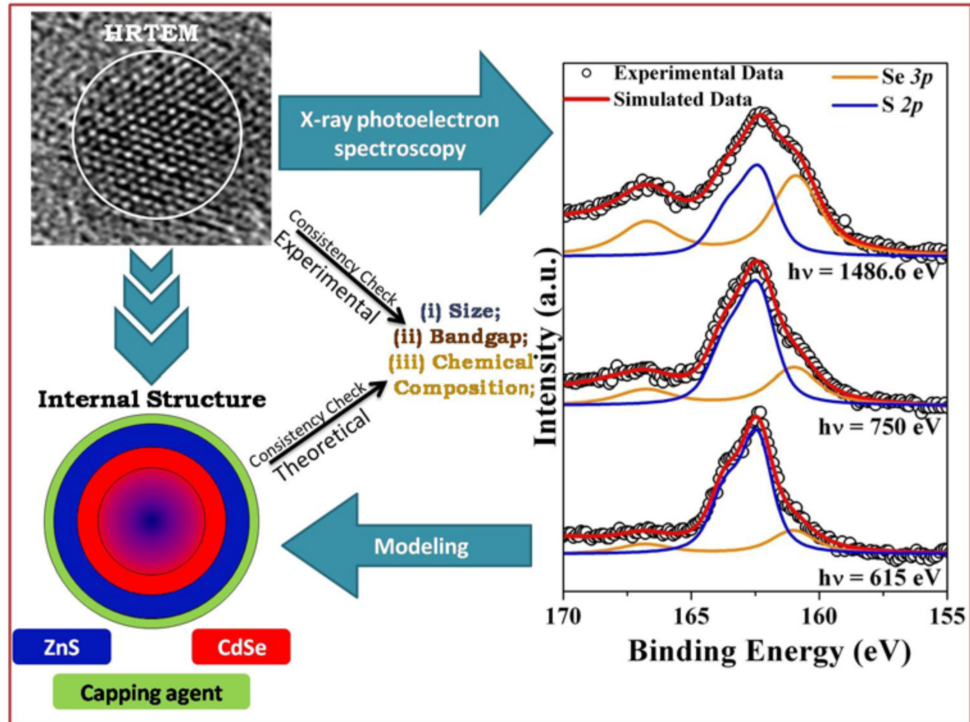
In recent times, semiconductor nanoparticles with diverse internal heterostructures have drawn immense attention due to their potential applications such as light emitting diodes and displays, optoelectronics, bio-sensing and bio-labeling. Although extraordinary properties have been achieved within various synthetic approaches, unfortunately very little is known about their internal structures responsible for such interesting phenomena due to the lack of a properly characterizing probe. Various forms of microscopy can only determine the overall size and shape but not the internal structure, particularly in presence of substitutional effects that interchange atomic positions of different elements. Given the fact that the typical nanoparticle of interest has sizes in the regime of 1-6 nm, it is evident that one needs a resolution considerably better than 1nm to probe such systems. X-ray photoelectron spectroscopy (XPS) is well established for providing information about composition in terms of intensity ratios of core level spectra of constituent elements in any sample. In this context, we recall the high surface sensitivity of XPS arising from an extremely short escape depth of the photoelectron, in the order of 0.5 nm. Moreover, a change in the photon energy enables one to change the escape depth controllably. XPS can determine the average composition from the intensity ratios of the core level spectra of different components. Thus, the intensity ratios of different core level spectra provide a certain weighted average value relevant for the thickness of the sample being probed at that photon energy. By increasing the photon energy moderately, one then averages the composition over a slightly larger thickness. Therefore, the change in the average composition with changing photon energy contains compositional information of the extra thickness of the sample that is added in the averaging of the composition with the higher photon energy. Thus, it becomes possible to extract the composition layer by layer of any complex material by systematically changing the photon energy for XPS. In essence, in place of a lateral resolution afforded by any microscopic technique, the vertical resolution (varying depth sensitivity) and composition sensitivity, both unique to X-ray photoelectron spectroscopy, can be used to unravel the compositional structure in such detail that is unique to this technique. It is obvious that the determination of the internal structure of the nanocrystal is made possible by a happy coincidence of the typical mean escape depth of electrons in XPS being in the same order as the size of these nanocrystals. Using extensive XPS experiments on ZnS-CdSe-ZnS quantum dot quantum well structure at VUV beamline of Elettra, recently we have been able to determine[1] in detail the internal hetero-structure of such complex nanoparticle for the first time. We have shown that such materials do not have the idealized sharp interface, instead forming a graded alloy structure, with significant and positive impact on its optical properties.

Published Reference: Investigation of the Internal Heterostructure of Highly Luminescent Quantum Dot−Quantum Well Nanocrystals, J. Am. Chem. Soc. 131(2009), 470.


HRTEM
X-ray photoelectron spectroscopy
Experimental Data
Simulated Data
Se 3p
S 2p
Consistency Check
Experimental
(i) Size;
(ii) Bandgap;
(iii) Chemical Composition;
Consistency Check
Theoretical
Internal Structure
Modeling
hν = 1486.6 eV
hν = 750 eV
hν = 615 eV
Intensity (a.u.)
170
165
160
155
Binding Energy (eV)
ZnS
CdSe
Capping agent