

Title: Reversed Nanoscale Kirkendall Effect in Au-InAs Hybrid Nanoparticles

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Metal-semiconductor hybrid nanoparticles (NPs) offer interesting synergistic properties, leading to unique behaviors that have already been exploited in photocatalysis, electrical, and optoelectronic applications. A fundamental aspect in the synthesis of metal-semiconductor hybrid NPs is the possible diffusion of the metal species through the semiconductor lattice. Here, we present a study of the structural evolution of InAs nanocrystals (NCs) during the addition, and solid-state diffusion of Au atoms. The importance of understanding and controlling the co-diffusion of different constituents is demonstrated in the synthesis of various hollow structured NPs via the Kirkendall effect.

In this work, we used post-synthesis, room-temperature reaction between AuCl₃ and 5 nm InAs NCs to synthesize a series of Au-InAs hybrid NPs with different Au/InAs ratios. We employed time-resolved (TR) x-ray absorption fine-structure (XAFS) spectroscopy in conjunction with scanning transmission electron microscopy/electron energy loss spectroscopy (STEM/EELS) and TR x-ray diffraction (XRD) to investigate the real-time Au diffusion process in these InAs NCs.

By using TR XAFS spectroscopy, we monitored the diffusion process and found that both the size of the Au core and the extent of the disorder of the InAs shell depend strongly on the Au-to-NC ratio. We also determined, based on multi-element fit analysis of XAFS data, that Au diffuses into the NC via the kick-out mechanism, substituting for In host atoms: this compromises the structural stability of the lattice and triggers the formation of In-O bonds. Control experiments revealed no formation of In-O bonds and no changes to the InAs structure, thus directly linking the observed changes and the diffusion of Au. The final Au-InAs core-shell is composed of a crystalline Au core and a disordered porous shell, as directly observed by STEM. Relative changes of Au and InAs crystalline volumes were studied by XRD for the 1000 Au/NC sample by using the relative changes in the InAs/Au peak intensities as a function of time. This ratio was found to monotonically decrease with time, implying that the long-range order of InAs is reduced relative to the increase in Au ordering.

By combining the results of XAFS, XRD and electron microscopy, we correlated the changes in the local structure around Au, As and In atoms, and the changes in the overall InAs crystal structure. In the presented system the diffusion rate of the inward diffusing specie (Au) is faster than that of the outward diffusion specie (InAs), which results in the formation of a crystalline metallic Au core surrounded by an amorphous, oxidized InAs shell containing nanoscale voids. The formation of the above structure can be rationalized through a reversed Kirkendall effect. This study of diffusion effects in nanocrystals therefore has relevance to powerful concepts in solid-state nanochemistry related to processes of cation exchange, doping reactions, and diffusion mechanisms.

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