

Crystal Structure Transformation in the Synthesis of Heterostructured Nanoparticles Containing a Heterophase Homo Junction

D. N. Suriyawansa, C. R. McCormick, H. L. Young, S. K. O'Boyle and R. E. Schaak

Heterostructured nanoparticles composed of at least two phase-segregated materials, offer promising applications in semiconductor devices, optoelectronics, catalysis, and energy storage. These nanoparticles can be designed and synthesized via cation exchange reactions, a post-synthetic modification technique that replaces cations within an ionic nanocrystal with cations from solution while preserving the original morphology and crystallographic features. However, alterations in the crystal structure may occur due to shifts in the anion sublattice. Partial cation exchange replaces only a fraction of the cations, creating phase-segregated nanoheterostructures with distinct interfaces, based on intraparticle frameworks that define the spatial arrangements of the constituent materials. This study employed multiple cation exchange reactions to target the formation of a heterophase homo junction within a nanoparticle, interfacing hexagonally close-packed (hcp) roxbyite $\text{Cu}_{1.8}\text{S}$ with cubic close-packed (ccp) digenite $\text{Cu}_{1.8}\text{S}$. Starting with $\text{Cu}_{1.8}\text{S}$ (hcp) rods, a partial Ni^{2+} cation exchange generated a heterostructured particle with $\text{Cu}_{1.8}\text{S}$ (hcp) and Ni_9S_8 (ccp). Ni_9S_8 has a distorted ccp anion sublattice, which when subjected to a Cu^+ cation exchange, converted to digenite $\text{Cu}_{1.8}\text{S}$ (ccp), forming a nanoparticle that interfaces $\text{Cu}_{1.8}\text{S}$ (hcp) and $\text{Cu}_{1.8}\text{S}$ (ccp). This created a heterophase homo junction between two materials with nominally the same composition but different crystal structures. Using these nanoparticles as a template material, a subsequent Cd^{2+} cation exchange produced a heterophase homo junction of wurtzite (wz) CdS and zincblende (zb) CdS. UV-vis absorption spectra reveal an intermediate band gap for the wz/zb-CdS compared to wz-CdS and zb-CdS particles of similar shape and size, indicating distinct properties that differ from individual components. This unique interface likely promotes efficient charge separation and transport, potentially enhancing the performance of photovoltaic devices and photocatalysts.