

Tailoring the carrier localization regime in colloidal $\text{CuInSe}_2/\text{CuInS}_2$ core/shell nanocrystals

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Quantum confined semiconductor nanocrystals (NCs), frequently synthesized as cadmium- and lead-chalcogenides (CdX and PbX ; where $X = \text{S}, \text{Se},$ and Te), exhibit widely tunable size, shape, electronic, and emissive properties, that can be easily controlled via solution-based synthetic techniques. While lead- and cadmium-based materials have been extensively studied and well established, these heavy metal materials are highly toxic. As a benign alternative, ternary compositions such as copper indium chalcogenides (CuInX_2) are being investigated because of the comparable tunability of their optoelectronic properties throughout the visible to the near-infrared spectral window.[1] However, direct synthetic protocols for ternary NCs are limited because multiple precursor reactivities must be tuned simultaneously.[1] As such, due to these synthetic challenges, the optoelectronic properties are still poorly understood. Topotactic cation exchange reactions have thus emerged as an alternative synthetic route, due to the post-synthetic control over the composition with size and shape preservation, as the anionic sublattice remains unaffected. This results in otherwise unattainable NCs.[2] By employing cation exchange methods, we have previously been able to produce CuInS_2 (CIS) quantum dots,[3] and $\text{CuInSe}_2/\text{CuInS}_2$ (CISe/CIS) dot-in-rod heterostructures,[4] using partial, self-limited In^{3+} for Cu^+ cation exchange reactions, by taking advantage of the synthetic versatility of parent Cu_{2-x}S and CdSe/CdS nanocrystals. As the anionic sublattice maintains the original structure of the parent CdX NCs, previously studied products of cation exchanged CIS and CISe reactions were found to also exhibit the wurtzite crystal structure. However, bulk CuAX_2 materials generally exhibit the chalcopyrite crystal structure (a cubic structure closely related to zinc blende), while CIX NCs have been reported in wurtzite, zinc blende, and chalcopyrite structures.[5]

This study examines the carrier localization regime in ternary CISe/CIS hetero-nanocrystals. As such, a series of wurtzite and cubic CdSe cores, and CdSe/CdS core/shell nanocrystals with variable core diameter were synthesized (ranging from 2 nm to 5 nm) and shell thickness (2 to 6 CdS monolayers overgrown on each core size). Subsequently, these core NCs and core/shell heteronanocrystals (HNCs) were used as templates and converted to the CuIn analogues using a sequential cation exchange protocol (Cd^{2+} for Cu^+ followed by partial, self-limited Cu^+ for In^{3+}). In this way, we can effectively tune the band offset between the CuInSe_2 and CuInS_2 segments in the HNCs, thereby affecting the carrier localization and exciton lifetimes. We study these CISe/CIS HNCs with time-resolved photoluminescence decay measurements and find that the exciton lifetime depends strongly on the size/thickness of the different components, core and shell.

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