Engineering I-III-VI colloidal nanocrystals: an interplay between size and composition effects

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Ternary I-III-VI nanocrystals are candidates to replace cadmium- and lead-based chalcogenide nanocrystals as efficient emitters in the visible and near IR, but, due to challenges in controlling the reactivities of the group I and III cations during synthesis, full compositional and size-dependent behavior of I-III-VI nanocrystals has not yet been explored. We report an amide-promoted synthesis of various I-III-VI nanocrystals that enables independent control over nanocrystal size and composition (see Fig. 1). By systematically varying reaction time, amide concentration, and molar ratio of metal salts, we develop a predictive model for the synthesis and show that I-III-VI sizes can be tuned for a fixed I-III-VI composition while broad range of indium-rich compositions is accessible. [1,2]

We perform structural and optical characterization for representative Ag-In-Se, Cu-In-Se, Cu-In-Te, and Ag-In-Te compositions. [1-3] We observe conventional size effects for each ternary composition, such band gap broadening and blue shift of emission for smaller nanocrystal sizes (see Fig.1). We further report systematic composition effects for I-III-VI nanocrystals, including narrower band gaps for Cu-In-X nanocrystals than for the counterpart Ag-In-X materials or band gap broadening for Ag-deficient nanocrystal compositions. We investigate the compostion-dependent luminescence efficincy for the Ag-In-Se system and observe two peaks in quantum yield. We relate these optimal compositions to stoichiometries exhibiting defect ordering in the bulk. [2]

Independent composition and size control allows us to optimize luminescence properties to achieve a record quantum yield of 73% for Ag-In-Se nanocrystals and 60% for Cu-In-Se nanocrystals (see Fig. 1). [2,3]

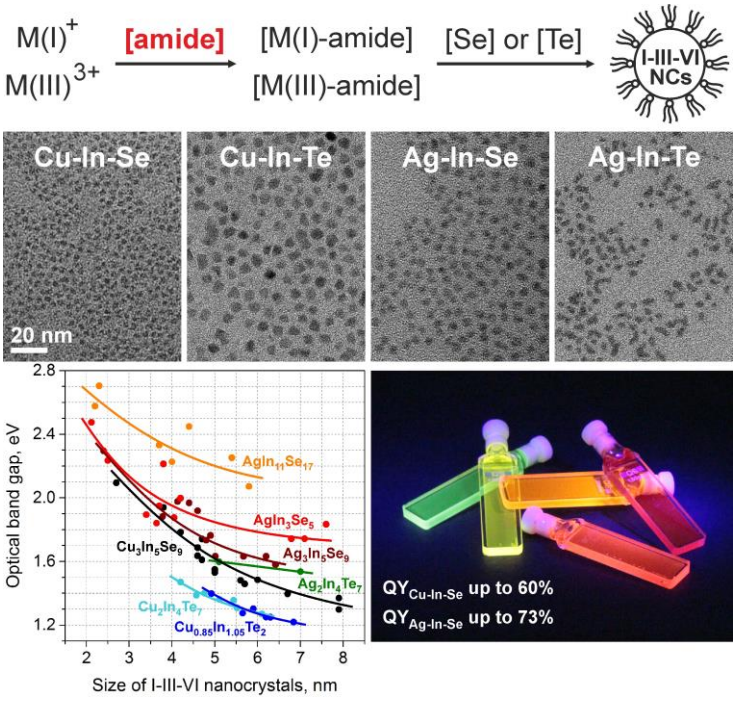

Figure 1 Various ternary I-III-VI nanocrystals can be prepared via an amide-promoted synthesis with independent size and composition control. Narrow size distributions (TEM images), size- and composition-dependent optical band gaps, and excellent emission properties are achieved

[1] O. Yarema *et al.*, *Chem. Commun.*, **2016**, *52*, 10878.
[2] O. Yarema *et al.*, *ACS Nano*, **2015**, *9*, 11134.
[3] O. Yarema *et al.*, *Chem. Mater.*, **2013**, *25*, 3753.