

# Title: Controlling Growth of Colloidal Cu doped ZnSe Nanostructures Using Magic Size Clusters

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Semiconductor nanocrystals exhibiting excellent electronic and optical properties serve as outstanding model systems for studying quantum confined size and shape effects and have promising applications in displays, solar cells, photocatalysis, sensing, printed electronics and in biomedicine. Shape control is an important knob for controlling their properties but so far it has been well developed mainly for heavy metal containing semiconductor nanocrystals, limiting their further wide-spread utilization. ZnSe is a representative of heavy-metal free and "Green" Zn-chalcogenide semiconductor materials. Herein, we investigated the mechanism of the growth of Cu doped ZnSe nanostructures with shape and size control via a novel synthesis route.

In this study, a series of Cu doped ZnSe nanostructures were synthesized using "Cu<sub>4</sub>" molecular clusters ([Cu<sub>4</sub>(SPh)<sub>6</sub>](Me<sub>4</sub>N)<sub>2</sub>) and ZnSe magic size clusters (MSCs). The shapes and sizes are controlled by heating process. Cu doped ZnSe nanostructures were characterized by x-ray absorption fine structure (XAFS) spectroscopy at Cu, Zn and Se K-edge to detect the evolution of the nanostructures at local atomic-scale in synthesis. The transmission electron microscopy (TEM) and x-ray diffractions (XRD) were also performed to provide information on the morphology and crystallinity of these Cu doped ZnSe nanostructures.

The near edge x-ray absorption fine structure (XANES) spectra at the Cu K-edge show changes after "Cu<sub>4</sub>" clusters were added into ZnSe MSCs, most notably upon heating. On the basis of Cu K-edge extend x-ray absorption fine structure (EXAFS) data analysis, there is a strong Cu-S peak observed in both "Cu<sub>4</sub>" clusters and "Cu<sub>4</sub>" clusters mixed with ZnSe MSCs, while in hybrid NWs and ZnSe nanorods (NRs) the major peak at longer distance is attributed to Cu-Se pairs. It indicates that the entire Cu element was incorporated into the ZnSe NRs to form dopants in the formation of ZnSe NRs with "Cu<sub>4</sub>" clusters. The growth of ZnSe nanostructures from MSCs grow to NRs by heating the solution in synthesis is confirmed by the Zn and Se K-edge EXAFS spectra and TEM imaging. TEM studies also revealed the formation of a hybrid inorganic-organic nanowire, whereby the ligands form a template for self-assembly of ZnSe MSCs.

In conclusion, this novel synthesis method is demonstrated to tune the shape of ZnSe nanocrystals and furthermore provide a route for Cu doped ZnSe nanorods. The use of Cu<sub>4</sub> clusters provided also a unique opportunity to employ x-ray absorption spectroscopy (XAFS) for deciphering the changes in the local atomic-scale environment of the clusters and explaining their role in the process of the nanorods formation. Overall, the combined use of MSCs and clusters presented here opens a path for controlled oriented attachment growth of colloidal semiconductor nanostructures expanding the pallet of materials selection with obvious implications for optoelectronic and biomedical applications.

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