Surfactant-assisted Cation-exchange Routine Towards Brightly Luminescent $CuInSe_2/CuInS_2$ Nanorods

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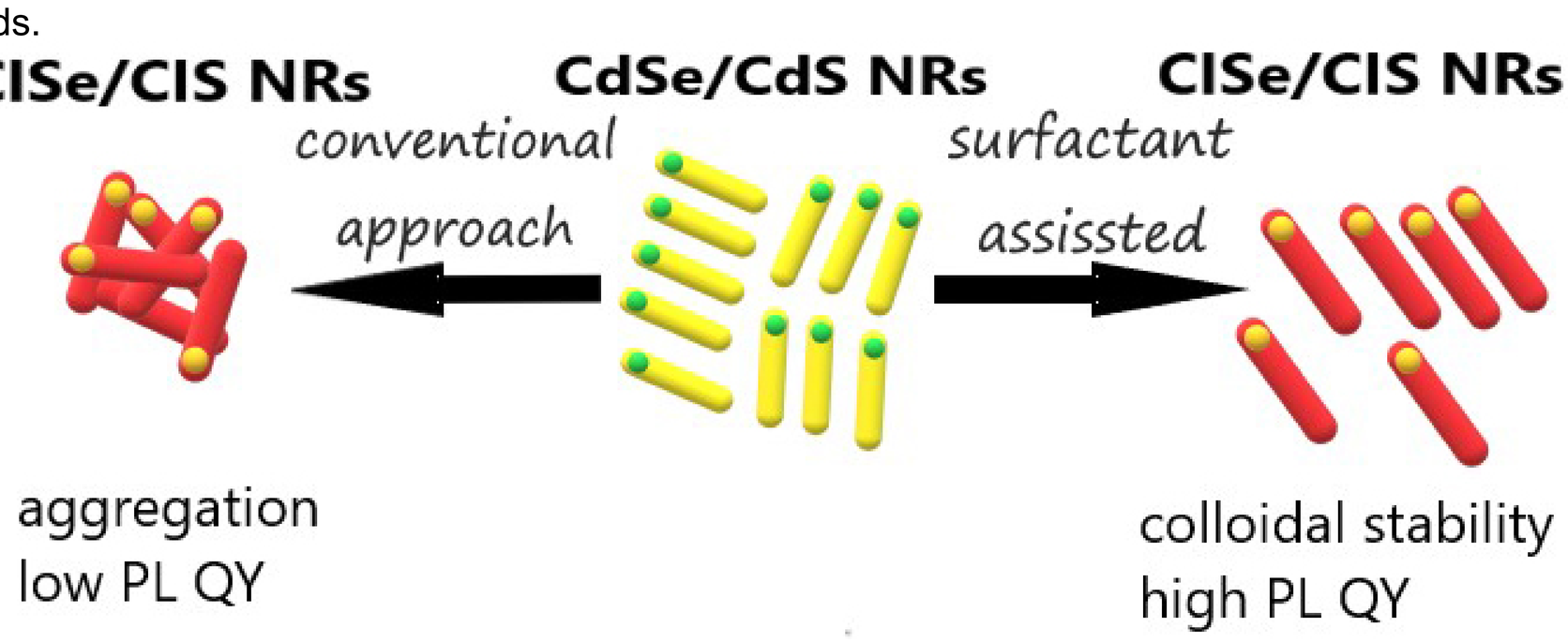
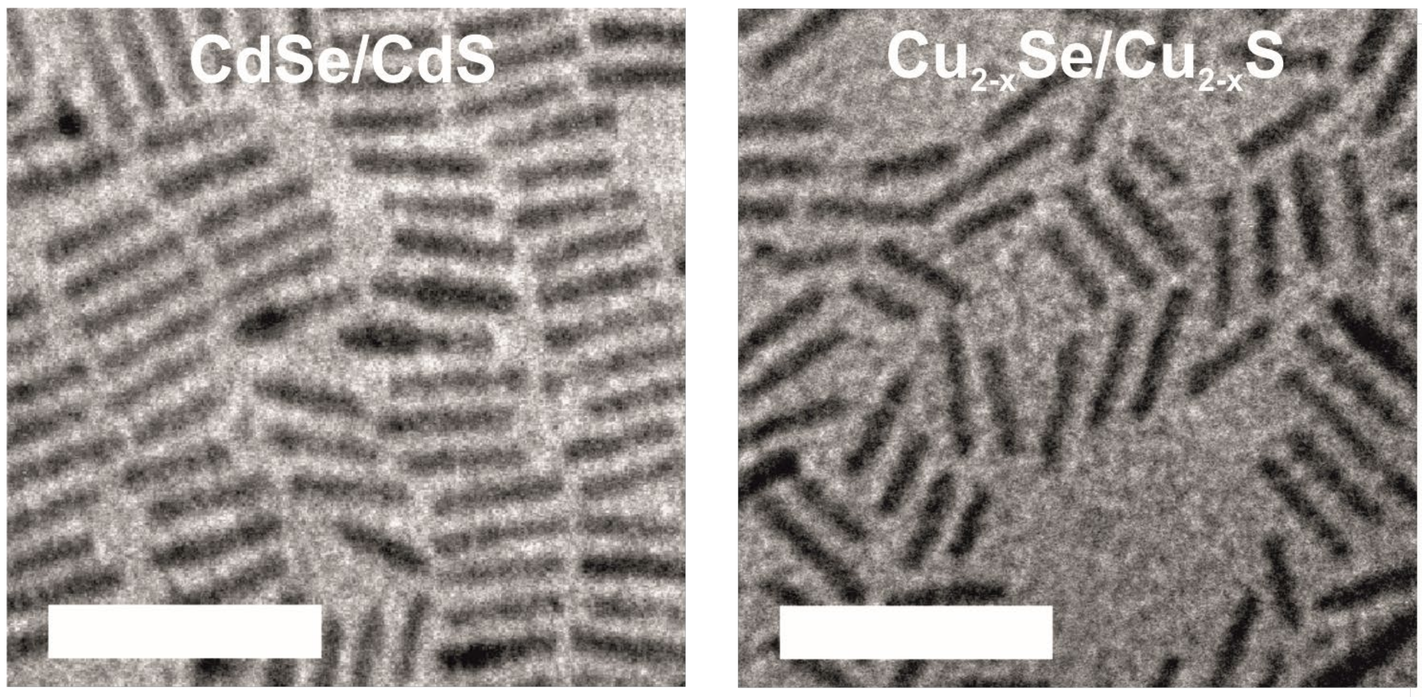
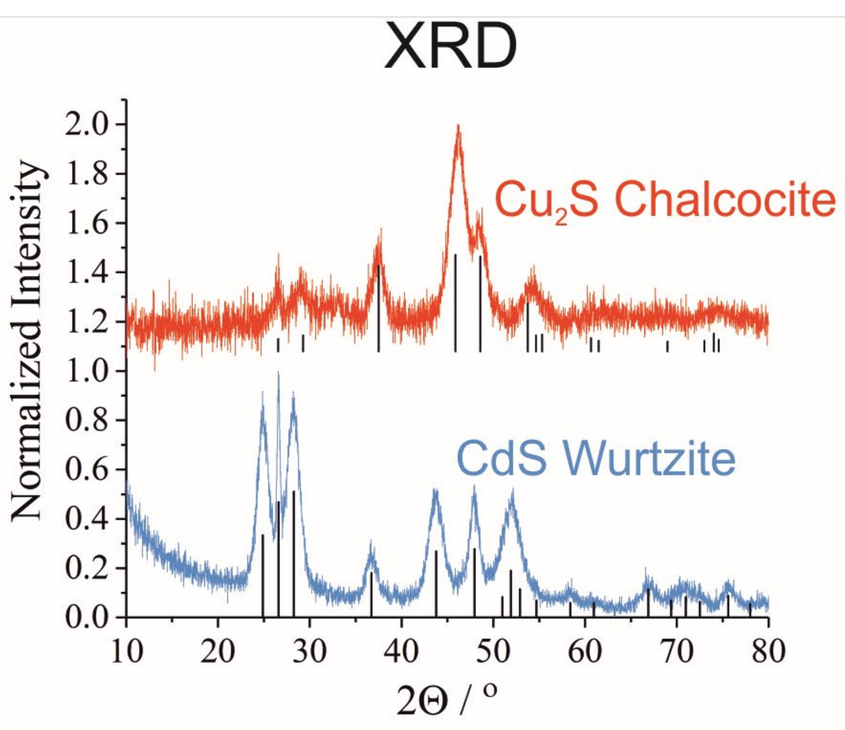
Cation-exchange is a powerful tool in researchers hands enabling to forge nanoparticles with any desired shape and composition that are not attainable by direct synthetic means. However, perturbations in cation sublattice create distortions and defects in the structure leading to material with rather poor optical performance. Here we present a cation-exchange procedure for preparing $CuInSe_2/CuInS_2$ nanorods starting from Cd-based ones with the PL QY of the final rods reaching 3.5% at the wavelength of 962 nm. Addition of dodecanthiol as higher affinity ligand to copper in comparison with hard phosphonic acid anions provides better colloidal stability resulting in better optical properties of the final rods.



Cd-to-Cu exchange

CdSe/CdS dot-in-rod core-shell heterostructure was a working horse for a number of studies serving as a starting point for further cation-exchange reactions as it was found easy to replace Cd ions with Cu in toluene-methanol mixture using copper acetonitrile complex. This allows preserving particle size distribution as well as the hexagonal symmetry of the crystal lattice.





Partial Cu-to-In exchang

Hexagonal packing observed in the obtained Cu-based rods enables one to get NRs with any desirable composition by replacing copper with other cations of interest. To get CuIn chalcogenides we implemented stoichiometric $InCl_3$-TOP complex to avoid cavity formation due to Kirkendall effect. However, conventional way already reported provides nanorods that form aggregates observed on TEM resulting in suppressed emission properties (PL QY <0.1). Here we introduced dodecanthiol surfactant, which possesses higher affinity towards nanorods surface in comparison to phosphonic acids, therefore, improving colloidal stability and enhancing PL QY in the NIR range (962 nm) till 3.5%, which is at the level of directly synthesized $CuInSe_2/CuInS_2$ quantum dots. This approach results in 1:1 Cu:In molar ratio, thus the stoichiometry is not perturbed with the introduced surfactant.