Synthesis and optical properties of nearly monodisperse near-infrared emitting $CuInS_2$/CdS Nanorods

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Given the ubiquitous examples of semiconductor nanorods synthesis, $CuInS_2$-based anisotropic heterostructures still lags behind in terms of shape/morphology/optical property control. In this study, we have developed a seeded growth approach towards core-shell CIS/CdS NRs with a narrow size distribution. Our synthetic pathway, depicted in Fig. 1, employs WZ CIS seeds obtained via a cation exchange starting from Cu2-xS QDs, followed by introduction of indium; they are finally overgrown with a CdS anisotropic shell. The WZ phase of CIS cores has enabled deposition of an elongated CdS shell, while avoiding formation of other possible competing morphologies such as tetrapods. The rod-like CdS shell could be formed on a variety of seed sizes (1.9-3.7 nm) preserving the narrow size distributions of the resulting core/shell NRs in terms of both the lengths and widths (Fig. 2). Also, incorporation of Zn into the CIS QDs did not perturb the morphological uniformity of the resulting rods. The aspect ratio of the obtained NRs could be tuned from 3.5 to 6.3 by increasing the reaction temperature. The NIR emission of the CIS samples spanning 760-900 nm with PL QY of 15-30% exhibited a blue-shift (20-80 nm) upon CdS shell growth, with the magnitude of this shift depending on the size of starting seeds and on the thickness of the shell as a result of CIS core etching, as confirmed by ICP-AES. Long radiative lifetimes were consistent with the quasi-type II heterostructure, where the lattice strain between core and shell slightly shifted the band alignments via conduction and valence band deformation potentials. The deposition of the CdS shell has been shown to increase the PL QY from 2-8% to 15-30% notwithstanding the influence of the moderate amount of strain introduced by the core-shell lattice mismatch. After introducing the shell, in all but one case the radiative rate increased while effective non-radiative rate decreased, with both factors jointly increasing the PL QY. The reduced effective non-radiative rate was attributed to the passivation of the core/shell interface. Further improvement of the NIR PL of the core-shell NRs was enabled by using CIZS cores alloyed with Zn, which resulted in high PL QY for their near-infrared emission (peaked at 772 nm) reaching 45%. Thus, synthetic approach presented in this study allows for fabrication of anisotropic CIS-based NRs with a strong NIR emission, which can be used for applications in the areas where charge separation is of great importance, as they have long exciton radiative lifetime, thus providing enough time for the extraction of the excited carriers. Another useful feature of these NRs lies in the high degree of their uniformity, enabling fabrication of densely packed films for the future eventual use in devices, because NR assembly is very sensitive to size polydispersity.

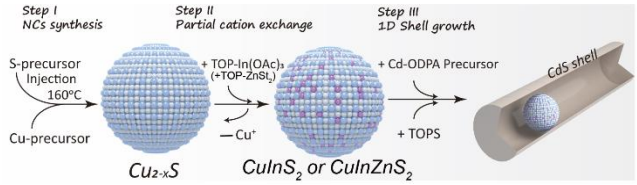

Figure 1. Illustration of the three-stage synthesis process of CIS/CdS nanorods consisting of hot-injection synthesis of $Cu_{2-x}S$ QDs, followed by converting them into CuInS2 by cation-exchange means and anisotropic CdS shell deposition at 350-380 °C via seeded-growth.

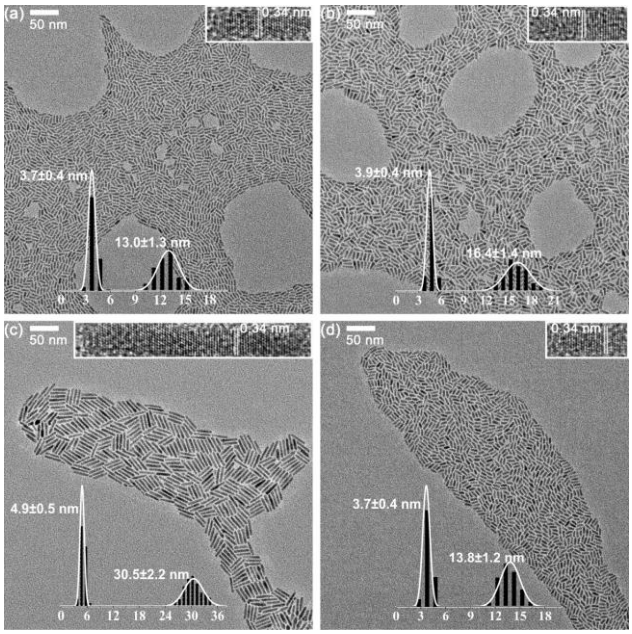

Figure 4. (a) and (b) TEM images of the CIS/CdS NRs, obtained from the 1.9 and 3.7 nm CIS seeds, respectively. (c) and (d) TEM images of 2.5 nm CIS/CdS and 2.5 nm CIZS/CdS NRs, synthesized at 380 °C and 350 °C, respectively. Insets in all four frames show HRTEM images of the respective NRs. Size histograms for lengths and widths of NRs are superimposed on each TEM image.