NIR-emitting Cu-In-Se-based quantum dots via cation exchange

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With the discovery of the copper chalcogenide-based ternary and quaternary colloidal nanoparticles, such as Cu-In-S(Se) (CIS(Se)), Cu-In-Zn-S(Se), Cu-Zn-Sn-S(Se), promising novel nanomaterials for applications as light absorbing layers in solar cells and as fluorophores for bio imaging and white LEDs fabrication were born. In contrast to the heavy-metal containing nanoparticles their advantage consists in their low-toxicity giving them permission to widen the range of applications. In particular, it makes possible in vivo imaging of biological processes facilitated by their fluorescence matching biological imaging window from approx. 700 to 1000 nm (CIS(Se)). This spectral region is poorly covered by other NIR emitting quantum dots (QDs) which so far are limited by toxic materials such as PbA (A = S, Se, Te), InAs, Cd_3P_2 and $Cd_xHg_{1-x}Te$.[1,2]

To date the range of light absorption/emission of copper chalcogenide-based nanoparticles is limited by approx. 1000 nm (CIS(Se)). Therefore, by pushing the photoluminescence of these nanoparticles to longer wavelengths even more applications are expected. For example, CuInS(Se)-based particles can be employed as a material for optical amplifiers in telecommunication systems based on silica fiber technology.[3]

In this work, starting from highly copper deficient binary $Cu_{2-x}Se(S)$ nanocrystals[4], CISe(S)-based QDs were obtained via a partial cation exchange reaction leading to a more precise control over the size, the shape and the composition of the resulting nanoparticles, as compared to their direct synthesis. In order to improve the stability of these QDs against oxidation and to enhance their photoluminescence quantum yield the as-synthesized nanoparticles were covered by a wide-band gap semiconductor shell (ZnS or ZnSe) yielding the core-shell QDs (Figure 1).

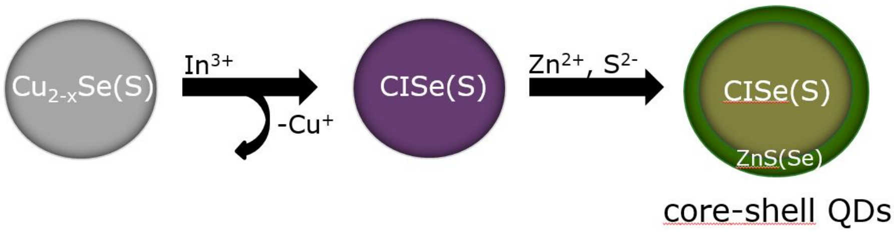

Figure 1. Scheme of the synthesis of CISe(S)-based nanoparticles.

Furthermore, we investigated in detail the dependency of the optical properties of the QDs on their size, composition and shelling method. As a result, we have achieved a wide range of the photoluminescence of these nanoparticles, whose maxima reach approx. 1300 nm. Thus, for the first time we demonstrate the emission of copper chalcogenide-based quantum dots extended so far to the NIR region, in particular, beyond their bulk band gap, possible owing to their complex exciton dynamics. The method developed in this work can be applied to the synthesis of the other copper chalcogenide nanomaterials, such as $CuInTe_2$, which is practically not investigated yet.

[1] Cassette, E. et al. *Chem. Mater.* **22,** 6117–6124 (2010).

[2] Aldakov, D. et al. *J. Mater. Chem. C.* **1**(24), 3756-76 (2013)

[3] Akkerman, Q. et al. *ACS Nano.* **9,** 521–531 (2015).

[4] Lesnyak, V. et al. *J. Am. Chem. Soc.* **137**, 9315-9323 (2015).