Insights in the synthesis of InGaP QDs and toxicological studies

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After the first publications about semiconductor colloidal quantum dots (QDs) in the early 1980s, they are now a well established class of nanomaterials with a wide application range. Cadmium based QDs were for a long time in the focus of research. Despite their unique properties and advantages compared to other QD compositions, the presence of the heavy metal Cadmium together with strict EU regulations concerning their use in electrical and electronic equipment is limiting their commercial utilization. This has drawn the interest to alternative materials with less toxicity but having similar photophysical features. [1]

The most promising candidate for the replacement are Indium based QDs. In particular InP nanocrystals with a bulk band gap of 1.35 eV and an exciton Bohr radius of ca. 10 nm allow for the tuning of photoluminescence (PL) emission from the visible to the near-infrared. In terms of stability the covalent character of InP compared to the ionic one of Cd based QDs is an advantage, but it has shown to hamper the synthesis of monodisperse QDs with a small PL linewidth and high quantum yield. In order to manipulate the size and shape of InP QDs and tailor their photophysical and optoelectronical properties different strategies were used. They range from the use of different types and concentrations of precursors, synthesis temperatures or post-synthetic manipulations like etching. [2] Another possibility is the incorporation of other elements within the InP core synthesis like Gallium. Using a GaP intermediate layer before growing a ZnS shell has been shown to increase the PL quantum yield, which has been attributed to reduced lattice strain and the removal of phosphor vacancies. [3,4] Different Ga precursors were investigated but a thorough investigation in terms of their reactivity, localization in the QD and influence on the photophysical properties is lacking to date.

In this contribution we will present the detailed investigation of the presence of two different Ga precursors within the InP core synthesis. Photophysical characterizations (steady-state and PL life-time measurements), transmission electron microscopy, XRD and EDX gave insights into the reactivity of the Ga precursors, the Ga localization in the InP core and influences on the photophysical properties. The variation of the precursor and surfactant concentration and the utilization of different ligands for the Ga precursor allowed tuning the PL emission towards the blue or the red. The strong increase in QY up to values of 75% and a size focusing effect were observed and made this approach valuable for the controlled synthesis of highly luminescent InP QDs for further applications.

Furthermore we will present new toxicological studies on InP-based QDs transferred to the aqueous phase via ligand exchange. We investigated the toxicity of two different core compositions and two different surface ligands namely glutathione and penicillamine in comparison to standard Cd based QDs with the same surface ligands. Despite the utilization of thick shells around the InP core the possibility of leaching ions from the core cannot be neglected but the intrinsic toxicity of Indium is lower compared to cadmium. [5] Remarkable differences were observed in the comparison of pristine QDs and QDs aged under irradiation with artificial sunlight. As model system we used human primary keratinocytes and investigated the cytotoxicity, cell proliferation, reactive oxygen induction and the genotoxicity. The picture was completed by X-ray fluorescence microscopy analysis of the localization of the QDs in the cells before and after aging.

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3) S. Kim *et al.*, *J. Am. Chem. Soc.*, **2012**, *134*, 3804.
4) J. P. Park *et al*., *Scientific Reports*, **2016**, *6*, 30094.
5) K. D. Wegner *et al*., *Chem. Soc. Rev.*, **2015**, *44*, 4792.