Preferential gallium for zinc cation exchange in In_xZn_yP nanocrystals

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InP based nanocrystals (NCs) are a promising low-toxicity alternative to cadmium-based NCs for light emitting applications. However, achieving near-unity photoluminescent quantum yields (PL QYs) and high photostability has proved a challenge for InP NCs. Some progress has been made by adding Zn^{2+} salts to the synthesis of InP NCs, which we have shown results in the the formation of In_xZn_yP nanocrystals and an improvement of their PL QY from < 1% (InP) to around 15% (InZnP) [1]. Further improvements in PL up to 50% have been reported by Kim et al. [2] by the addition of Ga^{3+} salts to In_xZn_yP NCs, which they attribute to the growth of a GaP shell *via* a cation exchange between Ga^{3+} and In^{3+}.

In this presentation we will argue that the PL enhancement afforded by Ga^{3+} is actually the result of a preferential cation exchange between Ga^{3+} and Zn^{2+}. This is based on the combination of optical spectroscopy, compositional analysis (ICP-AES) and electron microscopy to characterise the reaction between Ga^{3+} and In_xZn_yP NCs as a function of added Ga^{3+} (Figure 1). The results show a strong dependence on the zinc content in the starting nanocrystals, and suggest the gradual formation of a highly luminescent $In_xZn_yP/In_\alpha Ga_\gamma P$ core-shell structure *via* cation exchange. Finally, we will demonstrate the PL QY can be further increased up to 75% by further growth of an outer lattice-matched $ZnSe_zS_{1-z}$ shell, which also results in prolonged stability under UV illumination at ambient conditions. [3]

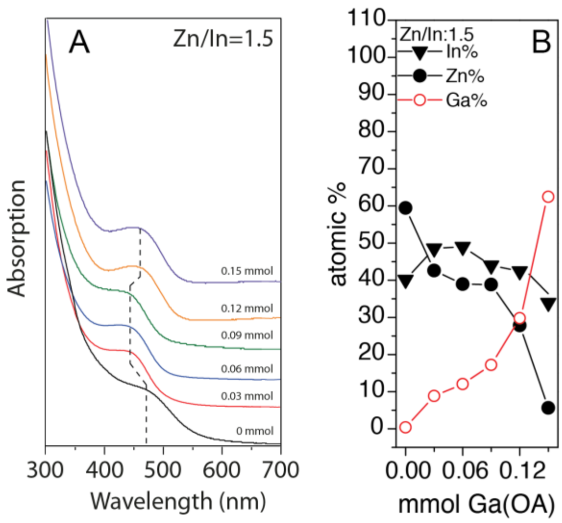

Fig. 1 (A) Absorbance of InZnP nanocrystals (Zn/In = 1.5, 0.12 mmol indium feed) as gallium oleate is added. Traces are offset with increasing gallium oleate addition. (B) Relative atomic percent of In, Zn and Ga for the same samples measured using ICP.

1) Pietra, F.; de Trizio, L. et al. *ACS Nano* **2016**, *10*, 4754–62.
2) Kim, S.; Kim, T.; et al. *Journal of the American Chemical Society* **2012**, *134*, 3804–3809.
3) Pietra, F; Kirkwood, N; de Trizio, L et al. *Manuscript in preparation,* **2017**.