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Firing up ceramic nanocrystals with photon upconversion

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This project combines the nanocrystal expertise of the De Roo lab with the photophysical and catalytic expertise of the Wenger lab.

$NaYF_4$ nanocrystals, doped with lanthanide ions such as Yb^{3+} and Er^{3+} are capable of upconverting infrared light into red, green and blue light. They are widely used in the biomedical field,[1] and have also been explored in the context of chemical catalysis. Complex nanocrystal architectures are possible with the $NaYF_4$ system, such as core/shell/shell nanocrystal with a precise positioning of dopants. However, the fluorides have been shown to have limited chemical stability in dilute aqueous media.[2] In addition, it is challenging to prepare sub 7 nm nanocrystals with high luminescence efficiency (relevant for biomedical applications),[3] and the different crystal phases further complicate the system. In contrast, the ceramic zirconium and hafnium oxide have a high chemical and thermal stability and are suitable host materials for lanthanides due to their low phonon energy and high band gap. However, the synthesis of these ceramic nanocrystals is lagging behind, precluding a precise control over nanocrystal architectures. While Eu^{3+} is almost quantitatively incorporated in the zirconia lattice, the other lanthanides are not. In addition, the photophysical processes in these oxide hosts are poorly understood. Recently, De Roo lab took a first step towards synthetic control by pioneering the epitaxial shell growth of hafnia onto zirconia cores, and pure zirconia onto europium doped zirconia cores.[4] The inert shell effectively deactivated loss mechanisms and increased the photoluminescence life time of the Eu^{3+} dopant. However, problems with independent nucleation of shelling materials persist.

In this project, we want to remove the bottlenecks for the use of upconverting and downconverting zirconia nanocrystals:
1. To improve lanthanide incorporation, we will manage the charge mismatch between Ln^{3+} and Zr^{4+} by co-doping and novel stoichiometries
2. We will develop novel chemical precursors with slower decomposition kinetics to control the shell growth and avoid homogeneous nucleation of shelling material. We aim at core/shell/shell architectures with independent control over dopant position.
3. Using advanced spectroscopy, we will demonstrate energy transfer between lanthanides and evaluate the effect of several architectures on the upconversion efficiency.
4. We will design and synthesize ligands that allow us to harvest the upconverted photons for driving chemical reactions.

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