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Nanoparticle growth probed by time-resolved luminescence spectroscopy

Aninda Chatterjee¹, Thomas Gustavsson¹, Akos Banyasz¹, David Carrière²

¹ *LIDYL, Laboratoire Interactions, Dynamiques et Lasers, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette France*

² *NIMBE, NIMBE, Nanosciences et Innovation pour les Matériaux, la Biomédecine et l'Énergie, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette France*

E-mail: aninda.chatterjee@cea.fr

Oxide nanoparticles (NP) are currently drawing a lot of attention because of their diverse applications such as catalysis, drug delivery, sensing and as luminescent materials.^[1] Clearly, optimizing the synthesis of such oxide nanoparticles is of high importance. In particular, the manufacturing of crystalline oxide nanoparticles in aqueous solution at room-temperature is industrially very appealing. However, this requires a detailed understanding of all the different phases involved in their formation from the initial homogeneous solution to the final crystalline mineral phase.

This complex process is loosely described by the classical nucleation theory, which relies upon a single step description of the formation of the primary centers ("seeds") by means of dynamic and stochastic association of the ions in solution. In this picture, the ions must overcome the free energy barrier before developing to a crystal of critical size which can grow to a mature crystal. However, there is evidence of the existence of non-classical intermediates like clusters, nanoscale amorphous precipitates, and other complex precursors in the liquid phase.^[2,3] The existence of a transient amorphous network with a two-level structuration was indeed confirmed by Fleury et al in the case of Eu:YVO₄ nanoparticles using In situ X-ray scattering and steady-state fluorescence techniques.^[4]

Indeed, the lanthanide luminescence can be used to monitor the growth of the nanoparticle under UV irradiation. The lanthanide does not absorb UV light directly, but the excitation energy absorbed by the matrix is transferred to the lanthanide (indirect excitation), thus acting as a very efficient phosphor. The luminescence intensity is thus regularly used as a direct sign of the NP formation. However, this approach is hampered by the continuously changing chemistry and morphology of the matrix itself, tuning both absorption and emission efficiencies in a non-trivial way.

In order to obtain a more detailed picture of the complex nucleation mechanism, including non-classical intermediates, we have chosen to develop a new approach, where not only the luminescence intensity but its lifetime is monitored during the nucleation process. The luminescence lifetimes of lanthanides are known to be very long, on the millisecond timescale, but are highly sensitive to the local environment (ligands, symmetry-breaking, nanoparticle size, etc.)

In order to follow the time-evolution of the nucleation process, we have monitored the luminescence decays of Eu³⁺ doped YVO₄ nanoparticles during the synthesis. By controlling the conditions, the nucleation rate can be tuned to proceed on a timescale from seconds to hours. Measurement of the luminescence decays of Eu³⁺ during such a "slow" synthesis show

not only the luminescence intensity but also the lifetime changes as depicted in the Figure.

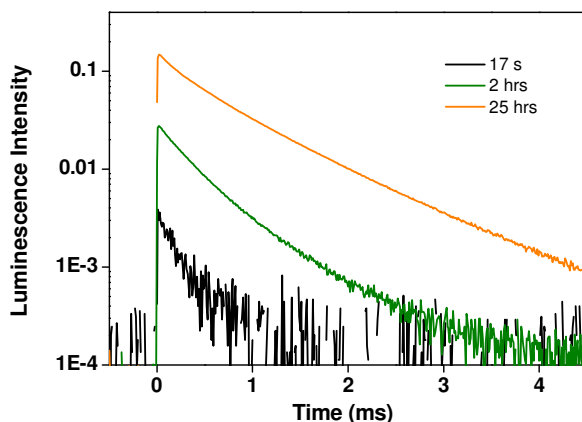


Figure. Luminescence decays at different reaction times from shortest time for V3 reaction condition of $\text{Eu}^{3+}:\text{YVO}_4$ nanoparticle synthesis.

The resulting luminescence decay curves are clearly non-exponential at all times, and could only be fitted with multi-exponential model functions. Interestingly, we observed that both the lifetimes as well as the relative contributions of the various components changes significantly over the monitored time interval. This evolution can be related to nanoparticle growth, but may also depend on the change of phase (amorphous to crystalline) as well as the chemical constitution of the matrix.

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