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Elucidating non-classical nucleation of nanocrystals from an amorphous intermediate state

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While nanoparticles are attractive because of their peculiar properties, their production remains a challenge. Their attributes mostly depend on size and surface state, but also on their microstructure. However, this structure (size, shape, porosity, crystalline quality) is currently only controlled via trial-error experimentations and poorly described by the only tool available, the classical nucleation theory (CNT), especially for oxide nanoparticles synthesised in water [1].

Luminescent, europium-doped yttrium vanadate (YVO4: Eu) illustrates nicely how important tuning the properties at the nanometric scale is. For light emission applications, a good crystalline quality and low surface to volume ratio is required, whereas porosity and high surface area will be key for chemical sensor applications [2,3]. This branching makes it crucial to understand the mechanisms of formation of these objects in order to have precise control on their structure and thus on their properties.

In this work, we focused on elucidating how crystalline YVO_4 is formed in water. A first striking result is that tuning the initial pH leads to two critical microstructures : (i) the “expected”[4], porous, one, with nanoparticles ~20nm wide composed of subunits of 2nm, (ii) a new, monocrystalline-like one, with particles 30nm large and no primary unit detected. To understand this difference, we conducted luminescence, pH, ICP-MS, and SAXS/WAXS/XRD studies during the reaction from reaction times as short as 5ms. In particular, we could show the existence of an amorphous intermediate state in both cases and its impact on the particles’ size and microstructure, and measure nucleation rates within the disordered network to improve nucleation theories.

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