

Flow supercritical synthesis of stable colloidal solutions of biocompatible InGaN nanoparticles

B. Dusolle,^{a,b} I. Bord-Majek,^a V. Jubéra,^b C. Aymonier^{b,*}

^aUMR 5210 – IMS – Laboratory for Integration: from Materials to System, Talence, 33405, France

^bUMR 5026 – ICMCB – Institute for Condensed Matter Chemistry of Bordeaux, Pessac, 33600, France

*cyril.aymonier@icmcb.cnrs.fr

1. Introduction

In_xGa_{1-x}N nanocrystals were synthesized using supercritical flow millifluidics to achieve non-aggregated particles which are dispersible and stable in hexane after purification, with a high production yield. Such materials are of great interest especially as visible light emitters for the fabrication of inorganic, solution-processed LED, as-known-as QLED (quantum-dot LED). Indeed, they represent a biocompatible alternative to more-investigated quantum-dot systems such as cadmium-based materials.

2. Materials and Methods

The reactor is a stainless-steel tube heated at 380°C in which the precursor solution and pure solvent were injected in a co-flow configuration, meaning the stream of precursor is injected through a smaller tube (1/16") placed inside the main tube (1/8") through which a stream of pre-heated pure hexane is injected (fig.1). This configuration helps for higher volume processing without any clogging due to heterogeneous crystallization on the tubes' walls, thus allowing production of enough materials for further characterization.

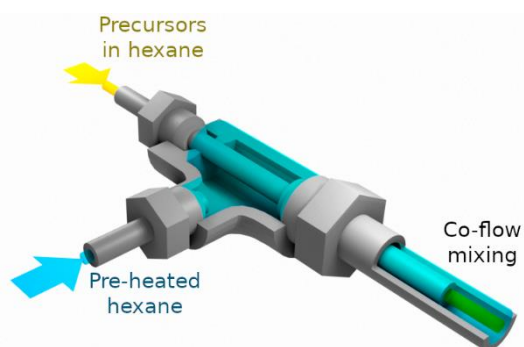


Figure 1. 3D modeling of a co-flow mixing system

Metallic cupferronate precursors were synthesized from indium and gallium iodides and cupferrons, re-crystallized and solubilized in surfactant. The resulting solution was then diluted in hexane and nitrogen source hexamethyldisilazane was added and injected via a HPLC pump into the reactor.

3. Results and discussion

Previously, the cupferronates' insolubility in hexane would call for the usage of methanol as co-solvent. In our case however, surfactants are used as solubilization intermediate to allow the use of hexane as the sole solvent. As compared with previous experiments using methanol¹, this new route results in higher crystallinity, non-aggregated particles in stable colloidal suspensions allowing the particle deposition as thin layer. Therefore, isolated nanoparticles could be observed via transmission electron microscopy (fig.2), leading to a better estimation of their size as well as the observation of atomic planes on a few particles, with inter-reticular distances coherent with targeted 25 at.%In nanoparticle compositions. The impact of residence time in the millifluidic reactor have also been investigated, highlighting the need for a longer reaction time to fully functionalize the particles with surfactants. Indeed, longer reaction time samples were more resistant to solvent wash and centrifugation thus facilitating nanoparticles purification, contrary to lower reaction time samples which needed month-long ripening at room temperature to obtain the same result.

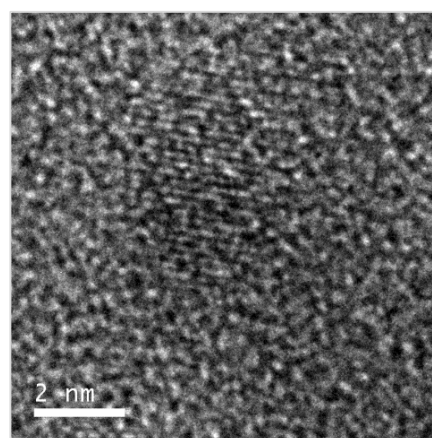


Figure 2. HR-TEM image of a single (InGa)N nanoparticle

Following this process, we report the synthesis of $\text{In}_x\text{Ga}_{1-x}\text{N}$ with $x = [0 ; 0.25 ; 0.5 ; 0.75 ; 1]$. Firstly, X-ray diffraction confirmed the dilatation of crystalline cells with incorporation of more indium. Then, our materials have been probed *via* fluorescence and spectroscopy in order to better understand their band structure and surface chemistry, which remain poorly known especially for high indium content phases.

4. Conclusions

Supercritical fluids technology has allowed for the continuous synthesis of high quality, solvent-dispersible (InGa)N nanocrystals, as opposed with classically used metal-organic vapor phase epitaxy techniques. This opens the way to an array of application using quantum-dots deposited *via* bottom-up techniques. Research is being led on the properties of different compositions of (InGa)N in order to fully understand the impact of surface ligands and crystalline defects on the fluorescence.

References

1. B. Giroire, A. Garcia, S. Marre, T. Cardinal, C. Aymonier, *Chem. Eur. J.* **2021**, *27*, 12965-12970.