

1. Crystal growth at the nanoscale

Organometallic precursors for nanoparticles of complex chemical composition

Our group develops the synthesis of semiconductor nanocrystals or quantum dots (QDs). The field of application of QDs is very wide (conversion of solar energy, biomarking, photodetection, screen, LED ...). These include the commercialization of a new generation of CdSe-based QDs in 2013. However, the use of QDs on a large scale is hampered by the problem of abundance and toxicity of the chemical elements used (mostly chalcogenides of Cd and Pb). In this field, our work has mainly focused on two aspects: the characterization of the surface at the molecular scale and the synthesis of QDs from innovative materials (germanium, indium phosphides and zinc).

a. Metal phosphides

While indium phosphide has many advantages for replacing CdSe (theoretical emissivity range 400-830 nm, low toxicity), the size control and optical performances remain below those of Cd or Pb systems. We have shown earlier that classical synthesis protocols lead to surface oxidation phenomena responsible for the self-inhibition of InP nanocrystal (NCs) growth ([JACS 2010](#), [JACS 2012](#)). More recently, we have shown that the presence of this oxide layer enables to increase the luminescence quantum yields (by minimizing the lattice mismatch between the core and shell) but this was detrimental to the sharpness of the luminescence peaks. (Coll. Z. Hens, Univ. Ghent, [Chem Mater 2018](#)). On this basis, we have developed new synthetic approaches from a more reactive indium precursor: indium tris (amidinate). This choice makes possible to drastically reduce the synthesis temperature (150 ° C, the lowest T ever described), thus leading to an oxidation-free surface allowing the growth of InP QDs. ([Chem Mater 2017](#)) and an unparalleled control over the attainable size range (Fig. 1).

Concerning zinc phosphide (Zn₃P₂), which appears to be the most promising material from a cost and environmental impact point of view, the stakes lie in the development of robust synthesis processes for obtaining stable and luminescent nanocrystals. We have developed two synthesis routes from new precursors leading to QDs with adjustable optical properties (luminescence between 650 nm - 730 nm), unequaled in the literature signal sharpness (90 nm) and luminescence efficiency (10%).

These advances have been made possible thanks to a fine characterization of the surfaces and interfaces, the nature of the ligands and their modes of interaction. In this context, we have highlighted the crucial role of the choice of solvents in the quality of QDs by identifying for the first time by solid phase NMR the presence of ligands of ethoxyl (CH₃CH₂O) and hydroxyl (HO) type (from the solvents used) on the InP nanoparticle (NP) surface ([PCCP 2016](#)). The extension of this work to TiO₂, ZrO₂, HfO₂ large gap semiconductor oxides was then carried out in collaboration with the groups of Z. Hens (Ghent Univ.) And J. Owen (Columbia University), showing the involvement of ligand coordination modes in catalytic processes ([ChemPlusChem 2016](#), [Chem Mater 2017](#)).

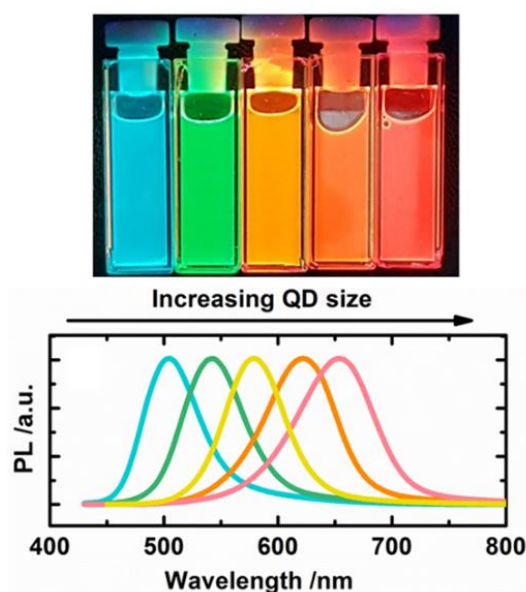


Fig. 1 : Spectra PL of InP QDs of variable size

b. Germanium metal germanide

Unlike conventional precursor-based pathways requiring hard synthetic conditions, we have been working on the design of molecular precursors (coll. D. Madec Coll., LHFA, J. M. Sotiropoulos and H. Martinez IPREM). This strategy allowed us to simplify the synthesis protocols (temperature reduction from 320 °C to 160 °C and broadening the range of usable ligands) to form Ge NPs (Dalton Trans 2015). As part of the ANR project "FeSi", we extended this method to the synthesis of iron germanide nanomaterials in the β ($\text{Fe}_{1.67}\text{Ge}$) phase (Dalton 2018) (Fig. 2). The choice of precursor substituents significantly influences the size, size distribution, and magnetic properties of the nanocrystals, with optimal control being obtained for the most labile substituent (consistent with DFT calculations)

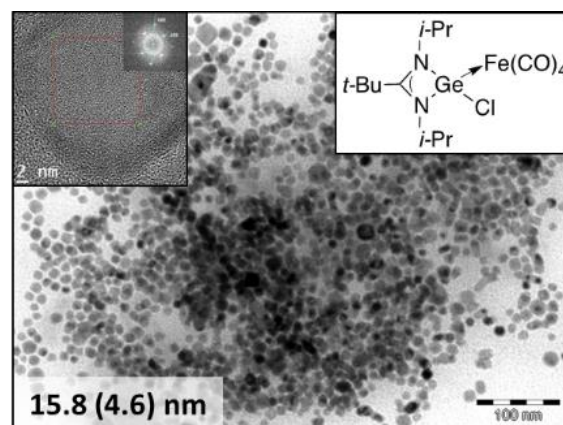


Fig. 2 : TEM micrographs of NCs of $\text{Fe}_{1.67}\text{Ge}$ synthesized from the complex in the inset.