METAL OXYSULFIDE NANOPLATES: GROWTH MECHANISM AND REACTIVITY, FROM LANTHANIDES TO TRANSITION METALS

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Summary: Metal Oxysulfides ($M_xO_yS_z$), in which the sulfur atoms are reduced (eg. S^{-II}), lie at the cross-roads of oxides (M_xO_y) and sulfides (M_xS_y): they present unique properties and still represent a synthetic challenge. The quest for efficient nanophosphors, with applications in lightening technologies and nanomedicine, raised the interest for oxysulfide nanoparticles in the 2000's. While bulk oxysulfides are usually prepared from the sulfidation of oxides at high temperature, Ln_2O_2S nanocrystals (Ln = lanthanide, Fig. 1) are formed in organic media below 350 °C.[1,2]

We produced metal oxysulfide nanoparticles by colloidal synthesis. We obtained unprecedented Ce_2O_2S nanoparticles as well as $(Gd,Ce)_2O_2S$ nanoparticles with Gd:Ce ratio from 0 to 100 %, forming a solid solution. The interest of cerium lies in its unique electronic properties in the lanthanide series. Ce_2O_2S is indeed the only lanthanide oxysulfide with a low bandgap (Eg < 2 eV), while the others are wide-gap semiconductors (Eg > 3 eV). Moreover, we evidenced that the 2-nm thick nanoplates showed a direct bandgap, instead of the expected indirect bandgap.[3]
Using Near-ambient-pressure XPS and XANES at S K-edge, we demonstrated that the nanoparticles were stable in air up to 40 % of cerium.[4] We then investigated the local structure of the nanoparticles, in relation with the presence of sodium in the reaction medium. At the time, sodium was considered a dopant in the structure.[2] Thermogravimetric analysis coupled to mass spectrometry was used to identify the surface ligands on the nanoparticles,[5] while SAXS-WAXS measurements evidenced the formation of a lamellar mesophase during the synthesis.[6] We confirmed by pair-distribution function analysis that Na was not a dopant in the nanoparticles. Lastly, we investigated the possibility to dope the nanoplates with molybdenum ions and form mixed compounds.

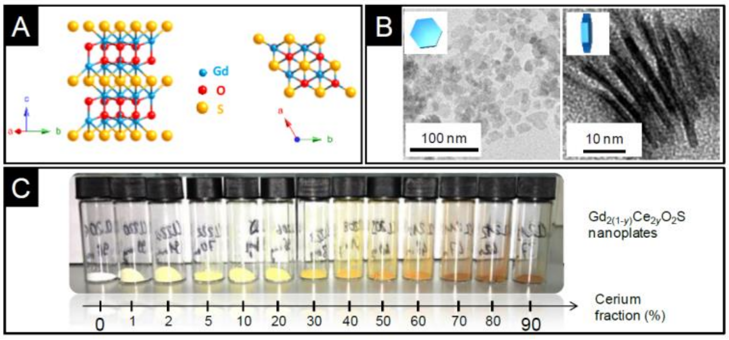

Fig. 1 (A) Gd_2O_2S structure. (B) Hexagonal nanoplates of $Gd_{1.25}Ce_{0.75}O_2S$. (C) Evolution of the powder colors along the series of $(Gd,Ce)_2O_2S$ nanoparticles.

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