Advanced nanostructured materials by design in supercritical fluids

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Cyril Aymonieriscurrently CNRS researcher at the "Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB)". He obtained his PhD in chemical engineering from University of Bordeaux (2000) where he focused on supercritical water oxidation of wastewater. He did a postdoctoral stay in Freiburg (2000-2002, Germany) with Pr R. Mülhaupt and Pr S. Mecking where he helped to develop novel approaches to design hybrid organic/inorganic nanoparticles. Now he is in charge of the department "Supercritical Fluids" of ICMCB (about 25 people). His current research interests are i) the study of the chemistry and nucleation & growth in supercritical fluids applied to the design of advanced nanostructured materials, ii) the study of materials recycling using supercritical fluids and iii) the development of the associated supercritical fluids based technologies. Cyril Aymonier has so far authored/co-authored 94 peer-reviewed journal articles, 6 book chapters and 15 patents. He was awarded by the CNRS bronze medal in 2011.
A strong collaboration exists with Pr Tadafumi Adschiri from WPI-AIMR (Tohoku University, Sendai) on the sustainable manufacturing of nanohybrid materials in the frame of the G8 Research Councils Initiative. This project allowed also developing interactions with the groups of Pr Masahiko Hirao and PrKohzo Itoh (University of Tokyo).

Abstract – The supercritical fluids method of advanced nanostructures manufacturing offers continuous, fast, scalable and sustainable routes towards high quality nanomaterials. Intermediate between solution based synthesis approaches and gas phase ones, the supercritical fluids routeis a versatile method already been used to synthesize various highly crystallineinorganic materials (oxides, metals, nitrides, etc.) with a control of composition, size and morphology [1, 2].
The use of sc-water as main solvent is now extended to other fluids (alcohols, NH_3, alkanes,… and mixture of them)to synthesize nanostructures. This variety of solvents opens avenue towards the use of numerous precursors for the investigation of a very rich chemistry; this means the use of more complex systems with an increasing number of parameters. We propose to highlight the chemistry and nucleation & growth in supercritical water / alcohol applied to the synthesis of $Ba_xSr_{1-x}Ti_yZr_{1-y}O_3$ ($0 \leq x \leq 1$ - BST, $0 \leq y \leq 1$ - BTZ) [3].The combination of *in situ* Synchrotron wide angle X-ray scattering (WAXS) with *ex situ* analyses as Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and high resolution transmission electron microscopy (HR-TEM) leads to a better understanding of the nanoparticle growth mechanism and so, to a better control of their physico-chemical properties. The densification of these unique BST, BTZ nanostructures by high pressure spark plasma sintering (SPS) conducts to the formation of reproducible and dense nanostructured ceramics with interesting ferroelectric properties [4].However, the use of surfactants to control morphology and surface properties remains essential. Therefore, although sc-water is a solvent of choice, the poor water solubility of some surfactants could require other solvents systems such as alcohols, which could themselves behave as surface modifiers. The influence of 7 different alcohols – MeOH, EtOH, PrOH, iPrOH, ButOH,

PentOH and HexOH - in alcothermal conditions (300 °C, 24.5 MPa) over CeO_2 nanocrystals (NCs) size, morphology and surface properties has been investigated. The crystallite size of the CeO_2 nanocrystals can be tuned in the range 3-7 nm depending on the considered alcohol, and their surface has been modified by these solvents without the use of surfactants. Mechanisms are proposed for the interaction of primary and secondary alcohols with CeO_2 surface and its functionalization during the synthesis [5, 6]. The understanding of the nucleation & growth of CeO_2 NCs in near- and supercritical alcohols is part of the collaboration with the group of Pr Adschiri [7]. The key role played by solvents will be also illustrated through the fast and continuous synthesis of GaN NCs in supercritical ammonia.

Finally, we propose to introduce the new methods we have developed coupling supercritical micro- and millifluidic for the design of advanced nanostructured materials [8]. Supercritical microfluidics was introduced few years ago to propose to improve the understanding and develop chemistries and processes for the design of advanced nanostructured materials through an access to *in situ* investigation and high screening capability [9]. As soon as the process is developed and the chemistry understood, the synthesis is made in millifluidic reactors to produce more materials for its characterization and its application. In this lecture, the interest of this original and efficient approach in Materials Sciencewill be illustrated with the formation of exciton luminescent ZnO NCs, efficient Pd-based nanocatalysts with tailored surface properties and QDs with different morphologies [10, 11, 12].

References

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