# Coupling supercritical micro- and millifluidic approaches for the continuous design of high quality nanostructures

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## ABSTRACT

Supercritical fluids offer continuous, scalable, fast and facile routes towards well-crystallized tailor-made oxide nanoparticles. This method has already been used to synthesize various inorganic materials (metals, semiconductors, nitrides, oxides, etc.) with controlled size, complex shapes and compositions. In the last 20 years, the use of sc-water as solvent was extended to other fluids to synthesize nanostructures (alcohols, $NH_3$, alkanes,… and mixture of them). 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. In order to have a better insight into these complex systems, 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* investigations and high screening capability. 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. We propose to present the interest of this original and efficient approach in Materials Science. This will be illustrated with the formation of exciton luminescent ZnO NCs and efficient Pd-based nanocatalysts with tailored surface properties. We propose also to highlight the chemistry and nucleation & growth in supercritical water / alcohol applied to the synthesis of $Ba_xSr_{1-x}TiO_3$ ($0 \leq x \leq 1$ - BST) or still $CeO_2$.

## INTRODUCTION

Supercritical fluids offer continuous, scalable, fast and facile routes towards well-crystallized tailor-made oxide nanoparticles [1, 2]. This method has already been used to synthesize various inorganic materials (metals, semiconductors, nitrides, oxides, etc.) with controlled size, complex shapes and compositions. In the last 20 years the use of sc-water as solvent was extended to other fluids to synthesize nanostructures, mainly $scCO_2$/alcohols (ethanol, isopropanol…), sc-MeOH, sc-iPrOH, water/alcohols (ethanol, isopropanol…), $scNH_3$ or sc-alkanes (hexane,…). This variety of solvents opens avenue towards the use of numerous precursors for the investigation of a very rich chemistry.

But when you speak about complex mixtures, you need to think first about thermodynamics. In systems like High-Pressure Optical Cells (HPOC), the pressure is directly controlled by temperature raise or decrease [3], *i.e.*, an increase of the temperature leads to an increase of fluid density. Although this approach provides very precise and reliable data, it lacks flexibility when targeting fast screening of the phase behavior. To overcome this limitation, we have developed a microfluidic approach coupled with modeling for the determination of complex mixture critical point [4].

After we propose to make a focus on the chemistry and nucleation & growth of nanostructures ($Ba_xSr_{1-x}TiO_3$ ($0 \leq x \leq 1$) - BST or still $CeO_2$) in supercritical water/alcohols mixtures (methanol, ethanol and isopropanol) but also in 7 different alcohols – MeOH, EtOH, PrOH, iPrOH, ButOH, PentOH and HexOH. Firstly, our pioneer works in supercritical water/ethanol mixtures for the formation of BST nanoparticles [5] have shown the possibility to obtain well-crystallized material at relatively low temperature (<400°C) recently confirmed with *in situ* synchrotron WAXS analysis [6]. Finally, these studies in water/alcohol mixtures brought us to alcohol (MeOH, EtOH, PrOH, iPrOH, ButOH, PentOH and HexOH) for the synthesis of $CeO_2$ nanocrystals. 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 [7].

The last section of this proceeding will illustrate how efficient is the coupling between advanced chemistry and advanced chemical engineering for the design of high quality nanostructures as defect free ZnO NCs [8,9] or still Pd NPs with controlled surface properties [10, 11].

## MICROFLUIDIC APPROACH FOR MULTI-COMPONENT P-T DIAGRAM

In order to construct a multi-component p-T diagram, our approach is based on the optical on-chip detection of bubbles and dew points (Figure 1) [4]. Initially, a fluid mixture with a particular composition is introduced at equilibrium in the microsystem, displaying liquid-fluid immiscibility, *i.e.*, droplets/bubbles are formed inside the microchannel and can be easily observed. Based on this point, the temperature was subjected to variations at isobaric conditions to find the bubble and the dew points. This means that the mixture turns to a fully miscible mixture by crossing the immiscibility / miscibility line in the p/T diagram. The mixtures critical locus curves can then be obtained through pressure-temperature (p-T) diagrams.

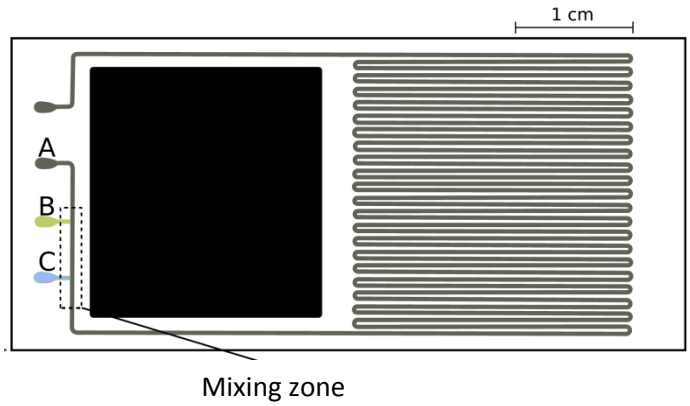


**Figure 1:** Scheme of the microfluidic-designed for the determination of multi-component p-T diagrams.

To construct these thermodynamic diagrams, movies were recorded with a Phantom® V9.1 at different capturing velocities, depending in the moment of analysis wanted.

With this approach we have studied the water/alcohol mixtures giving access to data like the critical coordinates of mixtures important for our investigations for the design of advanced materials: water/methanol (1/1): $T_c$ = 280°C, $p_c$ = 11MPa; water/ethanol (1/1): $T_c$ = 274°C, $p_c$ = 9MPa or still water/isopropanol (1/1): $T_c$ = 270°C, $p_c$ = 8 MPa.
When you know the thermodynamics of your mixtures, you can after study the chemistry and the nucleation & growth in these systems for the design of advanced nanostructured materials.

## CHEMISTRY AND NUCLEATION & GROWTH IN SUPERCRITICAL WATER/ALCOHOLS MIXTURES

Our pioneer works in supercritical water/ethanol mixtures were focused on the formation of BST ($Ba_xSr_{1-x}TiO_3$ ($0 \leq x \leq 1$)) nanoparticles. This technology exhibits very interesting characteristics such as the fast synthesis in continuous (few seconds) of high quality nanoparticles (well crystallized nanoparticles with narrow size distribution) with controlled composition ($Ba_{1-x}Sr_xTiO_3$ with $0 \leq x \leq 1$) at intermediate synthesis temperatures (< 400°C) with the use of non-toxic solvents (water, ethanol) (Figure 2). To understand the size variation according to the composition (from 20 nm ± 6 nm for $BaTiO_3$ to ± 16 nm ± 2 nm for $Ba_{0.6}Sr_{0.4}TiO_3$), *in situ* synchrotron powder diffraction was coupled with *ex situ* analyses such 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). The *in situ* analyses confirmed the influence of the strontium substitution on the growth of nanoparticles. The *ex situ* analysis evidenced the presence of surface –OH defects which decrease increasing the barium substitution with strontium. The synthesis mechanism being identified as following a sol-gel chemistry, the decrease of surface –OH will decrease the ability of the precursor to react at the surface of the particles and thus, limit the growth. Structural –OH defects were also identified and tended to decrease with the increase of strontium as well as the disorder due to titanium off centering at this size range.

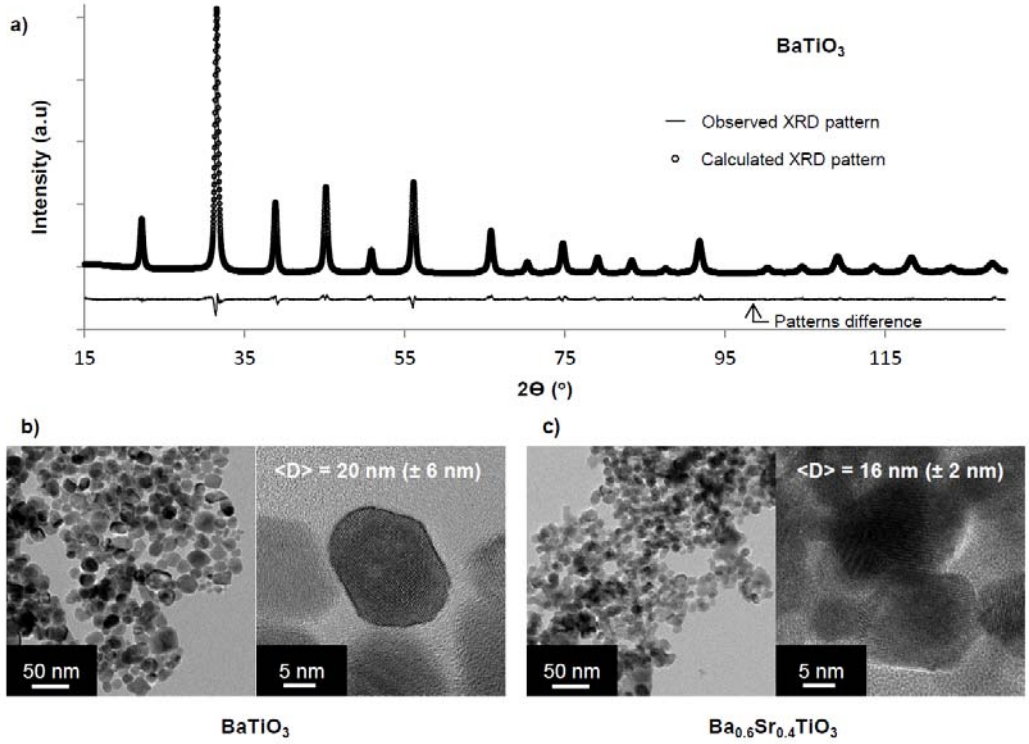


**Figure 2:** Continuous synthesis of BT - BST from alkoxides in supercritical water / ethanol mixture. BT synthesis: a) Rietveld refinement, b) HR-TEM pictures of $BaTiO_3$, c) HR-TEM pictures of $Ba_{0.6}Sr_{0.4}TiO_3$ (adapted from [12]).

These research works in water/alcohols mixtures brought us to investigate chemistry and nucleation & growth in pure alcohols, more precisely in 7 different alcohols – MeOH, EtOH, PrOH, iPrOH, ButOH, PentOH and HexOH – on the formation of $CeO_2$ NPs (size, morphology and surface properties). We obtained an unexpected result, the possibility to tune $CeO_2$ NCs size in the range 3-7 nm as a function of the carbon chain length of the alcohol. This is due to the interaction of alcohols with $CeO_2$ surface and its functionalization during the synthesis. This study allowed apprehending the role of alcohols during the synthesis opening new route to $CeO_2$ functionalization using supercritical alcohol derivatives.

The last step consists in coupling this very rich chemistry to advanced chemical engineering using microfluidics as a tool to develop the process and the materials.

## SEPARATION OF NUCLEATION & GROWTH AND FUNCTIONALIZATION

We introduced this concept few years ago [13]. Knowing that we can control nucleation & growth in the supercritical reactor, we proposed to spray the formed NPs into a functionalization vessel containing the surface modification agents. To have a better control on the strength of the interaction between the surface modification agents and NPs surface, we developed a coflow reactor thanks to microfluidics (Figure 3 –C1). Supercritical fluids processing within hydrodynamically controlled environments offered by high pressure / high temperature microreactors (namely supercritical microfluidics – SCμF [14]) has shown the opportunity to design excitonic luminescent ZnO NCs. Although supercritical microfluidics allows developing new processes for high quality NCs, production rates remain very low (few mg per hour).

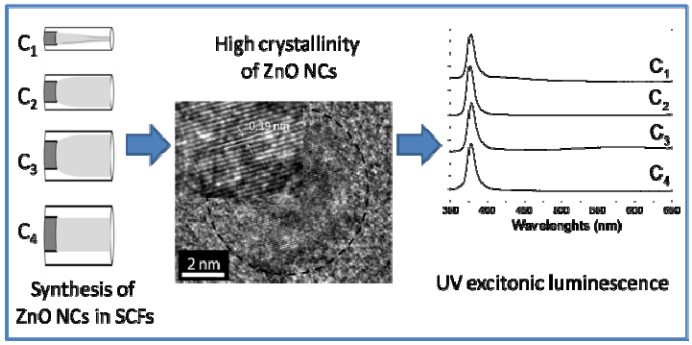


**Figure 3:** Evolution of an original supercritical fluidic device from micro- up to millifluidic scale correlated to ZnO NCs optical properties (adapted from 9).

Through the controlled modification of reactor's size of the set-up which allows obtaining larger quantities of ZnO NCs, we succeed to produce g scale of high quality ZnO NCs with optical properties better than the ones of bulk single crystals. Modification of hydrodynamic profile into reactors and its control results in the production of ZnO NCs with different morphologies such as spherical NCs, triangles and nanorods. Whatever the shape of NCs, the optical properties reveals a unique excitonic UV emission which confirms that the proposed synthetic route avoids the production of visible emission traditionally observed at this scale.
This original approach in Materials Science was also applied for the synthesis of highly active Pd NPs with specific surface properties.

## CONCLUSION

In the last 10 years the use of sc-water as solvent was extended to other fluids to synthesize advanced nanostructures with the use of more and more complex mixtures. This brought us to the development of a microfluidic approach coupled with modeling for the determination of complex mixture critical point. This is a powerful tool giving us the opportunity to use all the reaction media we want in respect to the chemistry we want to perform.

Supercritical water/alcohols were the first investigated mixtures to study the chemistry and nucleation & growth of nanostructures. Firstly, our pioneer works in supercritical water/ethanol mixtures for the formation of BST nanoparticles have shown the possibility to obtain well-crystallized material at relatively low temperature (<400°C) recently confirmed with *in situ* synchrotron WAXS analysis. Finally, these studies in water/alcohol mixtures brought us to alcohol (MeOH, EtOH, PrOH, iPrOH, ButOH, PentOH and HexOH) for the synthesis of $CeO_2$ nanocrystals. 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.

Recently we developed an efficient methodology in Materials Science coupling advanced chemistry and advanced chemical engineering for the design of high quality nanostructures illustrated with defect free ZnO NCs or still Pd NPs with controlled surface properties.

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