Sustainable low temperature wet chemistry route to crystalline inorganic nanostructures and their spectroscopic and structural characterisation

Silvia Gross,

Istituto per l'Energetica e le Interfasi, IENI-CNR, Dipartimento di Scienze Chimiche,

Università di Padova, and INSTM, UdR Padova, Padova, Italy

The paradigms of green chemistry are currently entailing all the fields of chemistry [1-4] and particularly inorganic chemistry represents an exciting playground for the design and optimisation of green chemistry -inspired and sustainable routes [5-6]. Environmentally friendly methodologies for the controlled synthesis of inorganic nanostructures are a noticeably stimulating research field since this encompasses not only the control of the final composition but also, and more importantly, a fine tuning of the obtained materials in terms of crystallinity (crystalline phase, crystallite size), shape, morphology.

Controlling size, shape and morphology, at the same time adopting mild conditions of processing parameters (mainly in terms of temperature and pressure) as well as safe, cost-effective, earth-abundant and common chemicals and solvents are relevant conditions to be met for sustainable and cost-efficient production of functional inorganic materials.

In this framework, wet-chemical routes are preferred to solid state ones for preparing inorganic crystalline materials since the liquid phase is more versatile with respect to the variation of structural, compositional and morphological features of the resulting compound materials. Furthermore, the molecular homogeneity of the starting solution or the microscopic homogeneity of the suspensions typically used in colloidal based methods are generally retained in the final materials.

In this contribution, selected synthetic routes for the low or room temperature of inorganic nanomaterials will be presented and described, with particular focus on hydrothermal synthesis [5,7], miniemulsion [5,8] and colloidal-based methods [5,6].

The last part of this talk will be instead devoted to outline the tight interplay among spectroscopic and diffraction-based methods for a sound and thorough characterization of inorganic nanostructures. Structural determination over different length scales combined with a detailed investigation of chemical environment and oxidation states of the involved species are important information to be collected in order to orient also the functional properties of the final nanomaterials.

As a working example, the combined use of XPS, XAS and Raman spectroscopies and of XRD to unravel the chemico-physical and structural features of a complex system such as the ceria zirconia so-called "κ-phase will be shortly discussed.

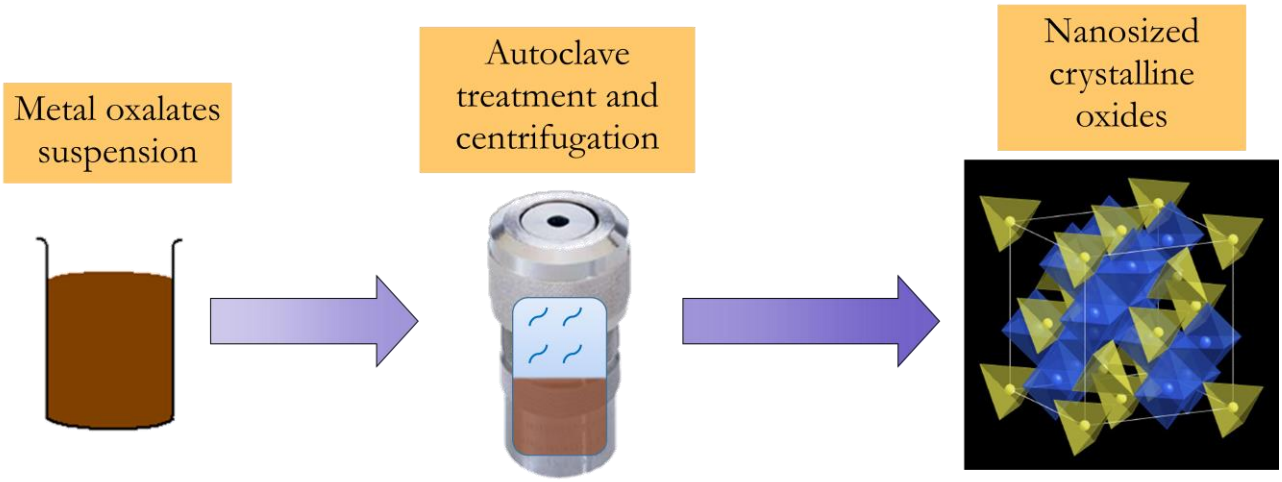

Fig. 1 Combination of coprecipitation of oxalates and hydrothermal treatment

References

1. Cushing, B. L., V. L. Kolesnichenko, et al. (2004). *Recent Advances in the Liquid-Phase Syntheses of Inorganic Nanoparticles*. Chem. Rev. 104(9): 3893-3946
2. Dahl, J. A., B. L. S. Maddux, et al. (2007). *Toward Greener Nanosynthesis* Chem. Rev. 107: 2228-2269.
3. Mao, Y., T.-J. Park, et al. (2007). *Environmentally Friendly Methodologies of Nanostructure Synthesis.* Small 3(7): 1122-1139.
4. Modeshia, D. R. and R. I. Walton (2010). *Solvothermal synthesis of perovskites and pyrochlores: crystallization of functional oxides under mild conditions*. Chem. Soc. Rev. 39: 4303-4325.
5. P. Dolcet, S. Diodati, M. Casarin and S. Gross *Very low temperature wet-chemistry colloidal routes for mono- and polymetallic nanosized crystalline inorganic compounds* 2014, J. Sol-Gel Sci. Technol.
6. S. Gross, *Sustainable and very low temperature wet-chemistry routes for the synthesis of crystalline inorganic compounds*, Chapter in *Green Processes in Nanotechnology*, Springer Verlag, in press
7. S. Diodati, L. Pandolfo, S. Gialanella, A. Caneschi and S. Gross *Green and low temperature synthesis of nanocrystalline transition metal ferrites by simple wet chemistry routes* Nano Res., 2014, *7*, 1027-1042
8. R. Muñoz Espí, C. K.Weiss, K.Landfester, *Curr. Opin. Colloid Interface Sci.*, 2012, 17(4), 212