Real time and in situ monitoring by Liquide Phase TEM of nucleation and growth processes of iron-based nanoparticles in organic media

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Thanks to the recent developments of the *in situ* TEM-based techniques allowing dynamical measurements in well controlled environments, it is now possible to obtain a direct and real-time insight on the reaction mechanisms that involve processes such as the aggregation or subsequent nanostructuration of complex molecules or individual atoms. This is particularly important for understanding and controlling the properties and structural characteristics of nanoparticles which are very sensitive to any subtle change in the reaction conditions.

Herein, we report the *in situ* TEM analysis of the nucleation and growth processes of iron-based nanoparticles by using the thermal decomposition method from iron stearate precursors in organic solvents.[1] 1 l of the reaction mixture (iron stearate, oleic acid and sodium oleate as ligands, octadecene as solvent) was deposited on the silicon nitride membrane of a "Protochips" liquid cell (Poseidon). The holder was inserted in a JEOL 2100F/Cs (S)TEM microscope operating at 200 kV and the continuous acquisition modes (in TEM and STEM) was used for acquiring dynamical events at various stages of the processes. The electron dose was calculated using the protocol described by Woehl et al.[2]

This work is one of the first studies reporting on the *in situ* monitoring of the synthesis mechanism of metal-based nanoparticles in an organic medium. The results are quite unexpected, in particular regarding the incipient steps of the particle formation. Using the energy provided by the electron beam for activating the process, we observed that the nucleation is preceded by the formation of some globular structures and then followed by the formation of crystalline nuclei within such globules. The observation of this pre-nucleation step provides a new insight on the thermal decomposition method so poorly understood until now. These structures can be interpreted as reverse micelles and/or vesicles. We attribute the presence of these architectures to supersaturation centers in the reaction medium enabling the nucleation of the seeds with a narrow size distribution.

Additionally, we have studied the growth process from the initial seeds to the final particles. By following step-by-step the evolution of the inorganic structures in the analyzed area, we demonstrated that the growth of particles occurs by a controlled aggregation process of smaller structures already present in the solution. The type of the solvent and the electron irradiation dose have also a considerable influence on the characteristics of the final particles in terms of size and general shape.

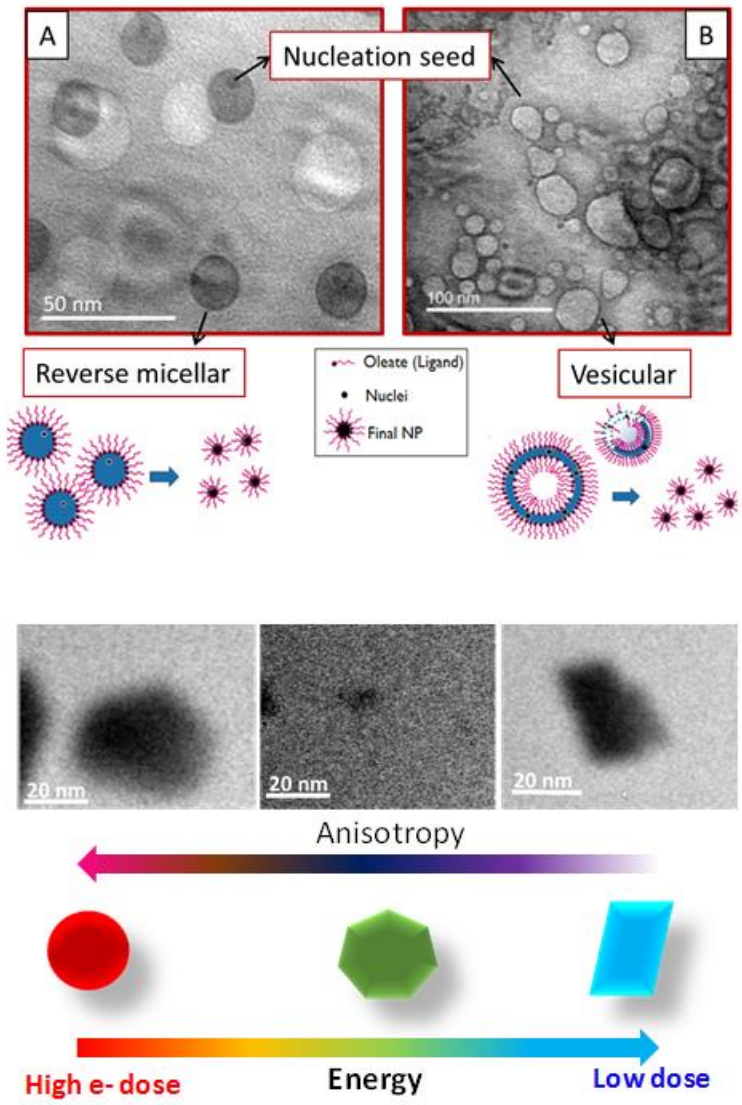

Figure : a, b) A snapshot on the nucleation step of iron-based particles in organic medium, illustrating the formation of globular structures in the TEM analyzed area and the nucleation of some crystalline seeds within these structures .c) The growth of an individual particle depending electron dose.

References:

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