2. Self-assemblies and new hybrid architectures

Growth and self-organization

a. Growth mechanism of cobalt nanorod mesocrystals

Cobalt NPs have very interesting magnetic properties that can be improved when they have an anisotropic shape (nanorods). By reducing under H_2 at 130 ° C a solution containing the precursor [Co {N (SiMe$_3$)$_2$}$_2$(THF)] in the presence of lauric acid (LA) and hexadecylamine (HDA), the formation of Co nanorod (NR) superlattices takes place directly in solution at the same time with the growth of NBs. To understand this complex process, unprecedent in-situ tandem EXAFS-SAXS experiments under pressure and heating were performed at the Argonne Laboratory (ANL) in United States as part of a bilateral collaboration (Coll J. Miller). One of the main questions concerned the moment at which organization takes place. The results unambiguously demonstrated that the NRs do not organize after their formation but in fact they organize from the beginning of the reaction and more precisely they grow while being organized (Fig. 1). These results show for the first time the simultaneous growth and organization of a phase analogous to smectic liquid crystal phases. (JACS 2016).

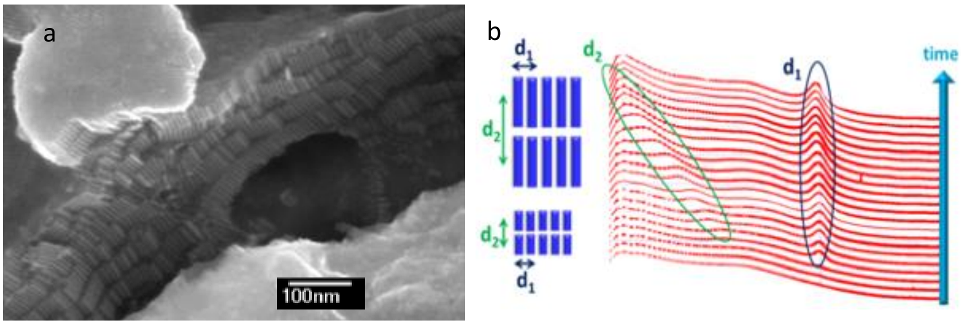
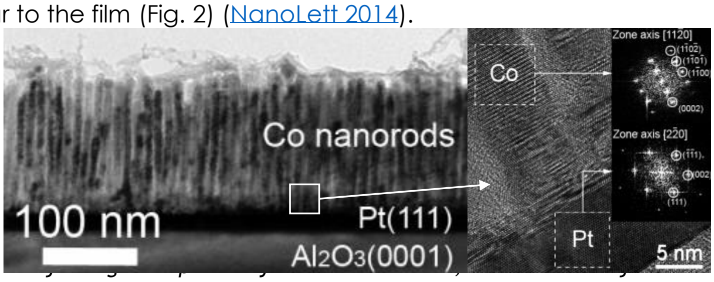


Fig. 1. (a) Co NRs organize in 3D super-lattices, (b) In-situ monitoring by SAXS the NRs growth process which proves that growth and organization are simultaneous. The peak at wide angles indicates the mean center to center distance between NRs of the same layer (d1). The peak at small angles corresponds to the distance between two NR layers of NBs (d2). The NR length increases with time.

b. Nanostructure superlattices on substrates

A monolayer of Co NRs organized perpendicularly to a flat support is a configuration relevant for ultra high density magnetic recording applications. In collaboration with the Nanomag group of the LPCNO, we have developed the elaboration of monolithic nanostructures on crystallographically oriented metallic supports. We have demonstrated that the reduction of a solution of the precursor [Co{N (SiMe$_3$)$_2$}$_2$(THF)], LA and HDA in the presence of a monocrystalline metal film surface allows the direct growth of nano-objects on that surface. This growth is epitaxial, and on crystallographically oriented supports exposing a surface of symmetry 6 leads to the formation of a network of perpendicular NRs or monocrystalline nanowires of Co of small diameter (<10 nm). The orientation of the NPs with respect to the substrate is perfectly defined, and the substrate-nanostructure interface is mechanically robust. Thanks to the common orientation of the easy magnetization axes of the nanowires, the lattice has a strong magnetic anisotropy perpendicular to the film (Fig. 2) (NanoLett 2014).



perpendicular to the plane of the substrate.

This method is applicable to other metals (Fe, Pt) on metal layers of different symmetry but also of different nature. In general, the shape of the nano-object that forms on a surface depends on the composition of the solution. Nevertheless, the symmetry of the surface as well as the epitaxial relationships between the surface and the nano-object are the parameters determining the orientation of the nano-object on the surface (ACS Nano 2015). In the case of platinum NPs we have demonstrated an epitaxial resolution of different nanostructures using a given crystallographic orientation support. Thus, from a solution that produces a mixture of nanostructures, the nanostructure that corresponds to the crystallographic orientation of the support can be selectively immobilized on the support. The orientation of the support dictates in this case, which nanostructures will be developed by epitaxy (Nanoscale 2018).