Tuning complex shapes in Pt(0) nanoparticles : from cubic dendrites to five-fold stars

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Synthesis of nanoparticles (NPs) exhibiting large surface-area-to-volume ratio has been a long-sought goal in developing various applications such highly active catalysts [1]. In addition to a large specific area, crystallographic planes exposed on the surface of the NPs are key parameters for the reactivity and selectivity of NPs in catalytic processes. Thus, intense researches have been devoted to the shape control of noble-metal nanocrystals. For instance for Pt based nanoparticles, dendritic nanostructures, branched-NPs, or multipods exhibit enhanced catalytic activities compared to their spherical counterparts. Such shape control could be obtained by manipulating the reduction kinetics through temperature, pH, ligands, or addition of small amounts of nucleating agents.

We will present complex platinum nanoobjects of unprecedented shapes (monodisperse cubic dendrites and five-fold stars) and the fine tuning between two growth mechanisms. An ex-situ kinetic study [2], followed by High Resolution Transmission Electron Microscopy (HRTEM), has evidenced two growth mechanisms based respectively on cubic or decahedral seeds leading to monodisperse cubic dendrites or five-fold stars. A complete study of their structural properties will be detailed.

A dendritic growth was observed at high Pt concentration ([Pt] > 5mM). The resulting objects were obtained quantitatively with a Pt yield over 95%. The most striking feature, compared to previously reported dendrites was their cubic contour (figure 1a). These dendritic structures are monocrystalline with an angular distortion of about 10° and present a highly faceted shape that we will detail (figure 1b).

At low Pt concentration ([Pt] = 2mM), star-shaped NPs were obtained. Samples were composed of nanocrystals exhibiting a well-defined morphology with ~ 20 % of 5-fold stars, ~ 70% of 3-fold stars (planar tripods) and ~ 10 % of multipods or undefined shapes. Figure 2a shows a high magnification image of a single 5-fold star. Figures 2b and 2c show HRTEM images of the branch tip and core of the star where a disclination is visible [3]. The branches are highly crystalline, exposing mainly {111} facets. These branches grow symmetrically along the twinning plane, from each corner of the central decahedra (figure 3).

In order to explain the two different shapes, the reaction rate has to be considered. A slow reaction leads to twinned seeds which evolve into planar tripods (3-fold stars) and 5-fold stars. A fast reaction leads to cubic seeds and thus to a dendritic growth.

References

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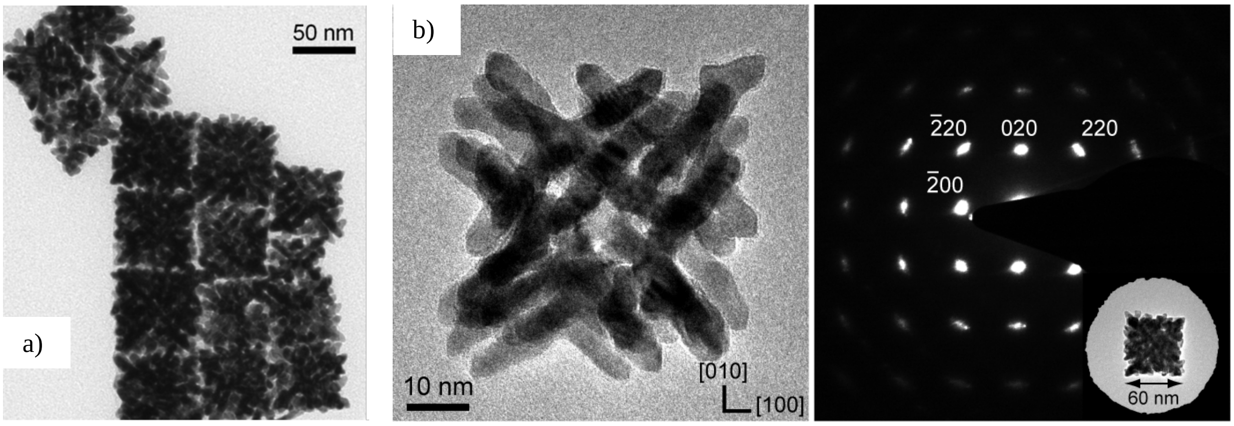

Figure 1. *TEM images of Pt dentritic nanoparticules: (a) low magnification TEM image, (b) and (c) TEM image on a dendritic structure and the corresponding diffractogram showing the monocrystalline structure*

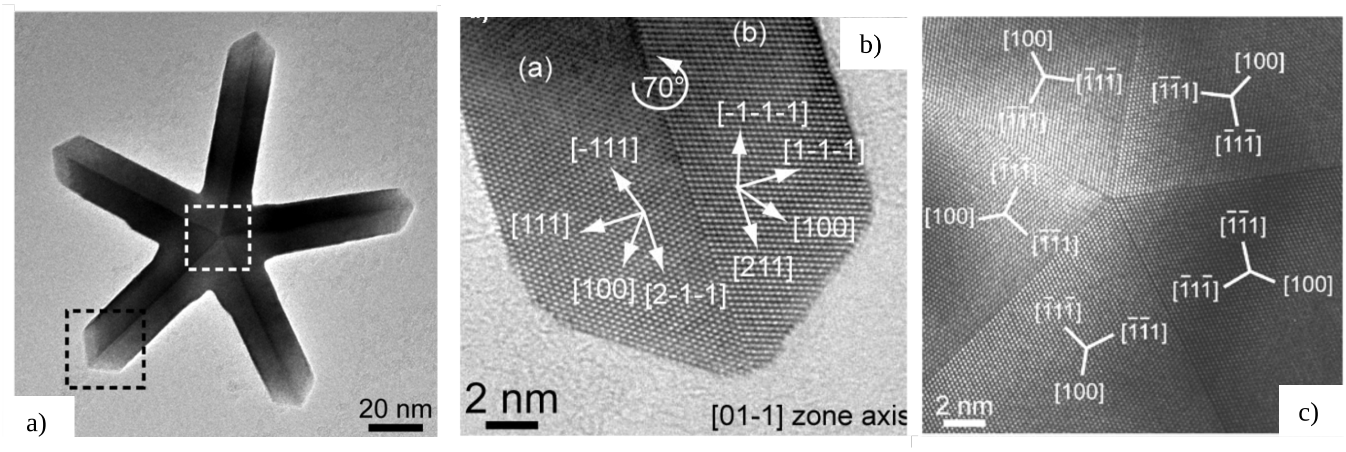

Figure 2. *(a) TEM micrograph of a single Pt 5-fold star, (b)and (c) HRTEM images of a branch tip and core as shown in figure (a) by black and white box respectively.*

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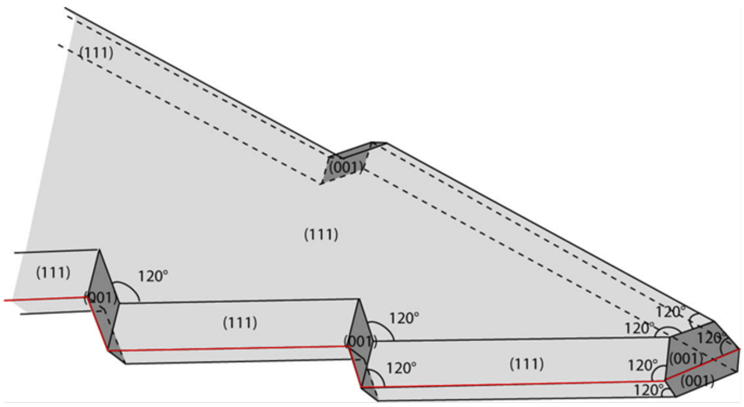

Figure 3. *Schematic view of the arms of 5-fold star displaying the corresponding faces and angles. The twinned boundary is represented in red.*