Structural Transition of PtAg nanoalloys: annealing effect on atomic ordering and segregation

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Metallic nanoparticles made of more than one element (i.e. nanoalloys) are developed because they can present synergetic effects which enhance a wide range of properties in many fields of science such as reactivity, magnetic storage or medical imaging. Taking advantage of both alloying and size effects, the so-called nanoalloys have considerably widened the technological potential of nanoparticles due to their tunability by size, shape and composition [1-4].

The structural landscape of bi-metallic nanoparticles is very rich: the structure and the state of mixing or segregation depend on multiple parameters leading to different structures (crystalline, non-crystalline, alloyed, segregated, core shell, onion like, Janus…). Obtaining a complete and precise description of a single particle, and checking its representativeness, remain challenging and the latest developments in electron microscopy could contribute to address this key issue.

The present study was done in an attempt to investigate the effects of composition, post –annealing treatment on the size-dependent atomic arrangement in Pt-Ag nanoparticles to study the phase diagram of this system at the nano-scale. The availability of sub-nanometer electron probes in a STEM and aberration corrected (Cs-corrected) high resolution transmission electron microscopy (HRTEM), ensure great capabilities for the investigation of size, shape, structure and composition.

PtAg nanoparticles were prepared by electron beam deposition of Pt and Ag on an amorphous carbon layer kept at room temperature during the deposition. The deposition rate was adjusted to reach an average composition of Ag-52at%. Post deposition annealing treatment were carried out under ultrahigh vacuum at 673K.

Figure 1 shows TEM and Cs-corrected HRTEM images of the PtAg nanoparticles prepared at room temperature and after a post annealing treatment reaching 673K. After the room temperature deposition the particles are crystalline and ramified. This is due to static coalescence effect: the consequence of high particle density on the carbon support. The post annealing treatment induces mobility of the atoms and particles and consequently Oswald ripening, dynamic coalescence and restructuration mechanisms leading to particles with a quasi-spherical shape. EDX analysis performed on single particles shows an evolution of the particles composition after the annealing process. Moreover, after the post annealing treatment some particles present an alternating contrast on HRTEM images. This is confirmed on HAADF STEM images as shown on figure 2. The combination of HAADF images and EDX analysis on single particles have shown that structural and chemical configurations depend on the composition showing alloyed or core-shell particles. Moreover a structural transformation from an alloyed disordered PtAg phase to an ordered L1_1 phase was observed. This L1_1 phase appears for a very narrow interval of composition and presents some internal strains.

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References:
Figure 1: TEM and HRTEM images of PtAg nanoparticles prepared at room temperature (a and b) and annealed at 673K (c, d and e). The histogram is done along the red line of the image e), it shows the alternating planes along the 111 direction.

Figure 2: STEM HAADF image of PtAg nanoparticles after the post annealing at 673K (a). Images at higher magnification (b and c) shows a particle with alternating plans along the 111 direction and multiply-twinned particle respectively. (d) HAADF image and the corresponding Ag (in red) and Pt (in green) EDX maps. The spectrum shows the Ag and Pt repartition along the white line in the HAADF image. It indicates no segregation in this particle.