Sputtering onto liquids: the behaviour of nanoparticles under thermal annealing

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Metal nanoparticles (NPs) are extensively studied due to their unique physical and chemical properties rising from their high surface area and nanoscale size. NPs are suitable candidates for various fields, including catalysis, imaging, medicine, energy production and storage, and environmental applications [1].

The synthesis of metal NPs is divided into two main groups, i.e., physical and chemical. Each of these methods has pros and cons; the physical approach allows the production of pure NPs while the chemical one allows the fine control of the size, dispersion, and shape [2]. In order to improve the synthesis of NPs, the combination of methods is of interest. The sputtering onto liquid is an approach combining both the physical and chemical ways. In this approach, the solid substrate conventionally used during the sputter deposition of a thin film is replaced by a liquid withstanding low pressure. Thus, the metallic target is sputtered in a vacuum chamber. The sputtered elements reach the surface of the liquid. Then, the nucleation and the coalescence of the species occur, and ultimately, NPs are formed [3].

Since the first reported use of this approach in 1974, more than 125 scientific papers have been published based on this process. Most of them highlight the sputtering of monometallic NPs and the influence of parameters on the resulting morphology of the NPs. One of the most used liquid host for sputtering process are ionic liquids due to the higher control of the NPs size and dispersion compared to oil. Moreover, ionic liquid interacts weakly with the sputtered species, so the purity of the obtained NPs is very high. However, ionic liquids are quite expensive and often hygroscopic. Thus, the replacement of ionic liquids by stable organic oils is favourable. The use of such oils raises interrogation concerning the interaction between the metal surfaces of NPs and the oil molecules.

In this context, we report on the synthesis of monometallic NPs (Cu and Au) and alloy NPs (Au/Cu) onto an organic oil, pentaerythritol ethoxylate (PEEL). Moreover, we reveal the behaviour of these NPs under thermal annealing. The synthesis of NPs has been performed by magnetron co-sputtering of a copper and a gold target onto PEEL; these two targets can be simultaneously sputtered to synthesize alloy NPs. Five samples were synthesized: one using only the copper target, one with only the gold target, and three samples with both targets while varying the sputter power on the gold target to achieve different gold concentrations within each sample. The resulting dispersions of NPs in PEEL were analysed using UV-vis spectroscopy, Transmission Electron Microscopy (TEM), and Small Angle X-ray scattering (SAXS). The hypotheses drawn during this study were supported by quantum chemistry-based calculations carried out at the DFT level [4].

The study reveals the successful synthesis of Au/Cu alloy NPs when using both targets. Moreover, the oxidation of the Cu NPs, obtained by sputtering only the Cu target, is reported. As highlighted in previous work [5], the mean diameters of alloy NPs appear to be smaller than the one of the monometallic NPs, i.e., 2 nm for Au/Cu NPs against 6 and 4 nm for Au and Cu NPs, respectively. We explain this behaviour by the interaction energy between each metal (and alloy) with the PEEL molecules.

Following the synthesis of the NPs by magnetron sputtering, solutions containing the NPs were further annealed at 200 °C for 5h with aim to increase the mean NP size. By selecting different intermediate annealing temperatures, we were able to follow the behaviour of each metal and alloy NPs during the thermal treatment in PEEL solutions. First, the gold NPs, which are initially 6 nm-in-diameter spherical NPs evolve to an interconnected ligament structure with a ligament size around 140 nm. Then, for NPs obtained by sputtering a copper target, the diameter evolves from 4 to 80 nm with almost no change in shape. Finally, the diameter of the spherical Au/Cu NPs grows, without change of shape, from 2 to 16 nm. Moreover, the alloy NPs are still composed of homogeneous Au/Cu alloy after annealing.

This study provides an essential insight into the sputtering onto liquids process to synthesize NPs and their development. One of the main issues raised here is the significant growth of the NPs when dispersed in PEEL and further annealed. However, the difference in affinity between the crystallographic facets of a metal NP leads to non-spherical structures after heating treatments.

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