

Insights into the synthesis of porous nanoparticles: from sputtering onto liquids to dealloying

Adrien Chauvin¹, Anastasiya Sergievskaya², Abdel-Aziz El Mel³, Cinthia Antunes Corrêa¹, Pierre-Yves Tessier³, Milan Dopita¹ and Stéphanos Konstantinidis²

1- Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 121 16 Praha 2, Czech Republic.

2- Chimie des Interactions Plasma-Surface (ChIPS), Research Institute for Materials Science and Engineering, University of Mons, 23 Place du Parc, B-7000 Mons, Belgium.

3- Université de Nantes, CNRS, Institut des Matériaux Jean Rouxel, 2 rue de la Houssinière, 44000, Nantes, France.

andrien.chauvin@karlov.mff.cuni.cz

Synthesizing high purity metal nanoparticles (NPs), having a well define shape and size distribution remains very challenging. Nowadays, NPs are mainly produced either by chemical or a physical methods. However, both methodologies suffer from drawbacks, i.e. the purity of NPs obtained by chemical methods is low while the control over the NP size, dispersion, and shape when using physical methods is limited [1]. In this context, the combination of both approaches seems promising to overcome these drawbacks and sputtering onto liquid appears to be an efficient alternative. In this process, ionized argon (ions) are accelerated from the plasma towards a metallic target to induce the ejection (i.e. the sputtering) of metal atoms or clusters into the vacuum chamber. These particles coalesce into NPs once they reach the liquid substrate [2]. This technique has been successfully used for the production of metal NPs and the simultaneous co-sputtering of two metal targets enabled the synthesis of homogenous alloy NPs [3]. Such alloy NP can be the dealloyed to make nanoporous NPs [4] with enhanced properties as, for example, in cancer therapy applications [5]. The dealloying, or selective leaching, deals with the removing of the less noble metal of an alloy to leave behind a skeleton made of the more noble element. This procedure has been investigated for thin films but not so much for NPs [4, 6]. In this contribution, we first present the production of Au-Cu NPs by magnetron co-sputtering of gold and copper targets onto a liquid substrate (pentaerythritol ethoxylate). Second, the coalescence of these NPs by thermal annealing is discussed because it is a necessary to get big enough NP to allow the dealloying process to occur. Finally, the formation of nanoporous gold NPs by dealloying is demonstrated. Overall, this study implies the use of transmission electron microscopy, small angle X-ray scattering, DFT calculations and UV-Vis absorption spectrophotometry.

[1] H. Wender, P. Migowski, A. F. Feil, S. R. Teixeira and J. Dupont, Sputtering deposition of nanoparticles onto liquid substrates: Recent advances and future trends, *Coordination Chemistry Reviews*, 257, 2468-2483 (2013).

[2] X. Carette, et al., On the Sputtering of Titanium and Silver onto Liquids, Discussing the Formation of Nanoparticles, *The Journal of Physical Chemistry C*, 122, 26605-26612 (2018).

[3] M. T. Nguyen, H. Zhang, L. Deng, T. Tokunaga and T. Yonezawa, Au/Cu Bimetallic Nanoparticles via Double-Target Sputtering onto a Liquid Polymer, *Langmuir*, 33, 12389–12397 (2017).

[4] X. Li, et al., Dealloying of Noble-Metal Alloy Nanoparticles, *Nano Letters*, 14, 2569-2577 (2014).

[5] J.-W. Xiao et al., Porous Pd nanoparticles with high photothermal conversion efficiency for efficient ablation of cancer cells, *Nanoscale*, 6, 4345–4351 (2014).

[6] A.-A. El Mel et al., Unusual Dealloying Effect in Gold/Copper Alloy Thin Films: The Role of Defects and Column Boundaries in the Formation of Nanoporous Gold, *ACS Applied Materials & Interfaces*, 7, 2310–2321 (2015).