

# Sputtering metals on liquid substrates for nanoparticle synthesis.

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## 1. Introduction

The combination of low-pressure plasma-based magnetron sputtering with liquid substrates that sustain vacuum is an efficient way to synthesize nanoparticles (NP) as reported in several studies e.g. [1,2]. This technology takes advantages of the fact that lots of materials can be sputtered, from pure metals to alloys or even ceramics. The argon gas can also be mixed with e.g. O<sub>2</sub> or N<sub>2</sub> to perform reactive sputtering and allow producing oxide or nitride metal compounds, respectively. Co-sputtering can be carried out as well [3]. Also, by using this method, synthesis routes involving chemical reagents are avoided and nanoparticles are directly collected by the liquid hence strongly reducing the risk of contact with the NP. Here, we briefly summarize our first study in this area. More detailed information can be found in the already published article [4].

## 2. Materials and methods

For the sputtering experiments, 4 ml of liquid was poured into a crucible located 15 cm from the magnetron cathode. We used either a 5.1 cm in diam. Ti or a 7.5 cm in diameter Ag target. The power density was ~0.4 W/cm<sup>2</sup> for the Ti target and ~1 W/cm<sup>2</sup> for the Ag target. Both metals were sputtered in an Ar plasma. For Ti, a total pressure of 0.7 Pa was used while for Ag, the pressure was 1.3 Pa. Two host liquids were chosen: 1-Butyl-3-methylimidazoliumbis(trifluoromethanesulfonyl)imide (BMIMTFSI) ionic liquid (IL) and pentaerythritol ethoxylate (PEEL).

Calculations at the Density Functional Theory (DFT) level (SIESTA 4.0 code [5]) were carried out to get further insights into the chemical interactions between the PEEL molecule and the surface of different nanoparticles.

The solutions loaded with NP were analyzed by UV-Visible spectrophotometry (UVS). The morphology of the particles was monitored using a Transmission Electron Microscope (TEM) and Selected Area Electron Diffraction (SAED).

## 3. Results

Ti was sputtered over the PEEL solution using an Ar plasma. The presence of a film on the surface of the liquid was observed as the sample was taken out the chamber. This film remained on the surface of the liquid when stored several days inside the vacuum chamber, in argon atmosphere. However, the film broke down as the chamber was vented (and the film allowed to interact with air) and film debris precipitated at the bottom of the flask. After a few days, the film solid residues could not be distinguished by naked eye.

If the chemical interaction between the sputtered Ti atoms and the PEEL oil is not favourable, one may expect the solvation of the sputtered metal atoms to be prevented or the solvation process to be very slow and the sputtered metal atoms impinging on the surface of the PEEL solution to behave as if they were landing onto a solid surface. On the other hand, due to the very good affinity of Ti for O, the film gets oxidized in contact with air during venting. At this moment, the affinity of the PEEL molecules for the TiO<sub>x</sub> surface is enhanced and solvation of the multitude of islands forming the film may eventually start. DFT calculations highlight that the bidentate anchoring of the PEEL on the TiO<sub>2</sub> surface is the most favourable situation as compared to an interaction with pure Ti surface. Calculations also show that Ag does not interact favourably with the PEEL. However, the interaction of Ag<sub>2</sub>O and AgO is more favourable.

The solution of PEEL treated by the Ti-sputtering plasma is analysed by UVS. Absorption data are reported on Fig 1. The shoulder appearing at ~360 nm is the signature of the presence of TiO<sub>2</sub>-NP inside the liquid. The shoulder is more pronounced as the amount of sputtered metal increases, i.e., the treatment time is increased. TEM analysis show that the NP are anisotropic and faceted. SAED revealed that the NP are crystallized and made of anatase. The NP have variable sizes, ranging from ~30 to ~150 nm.

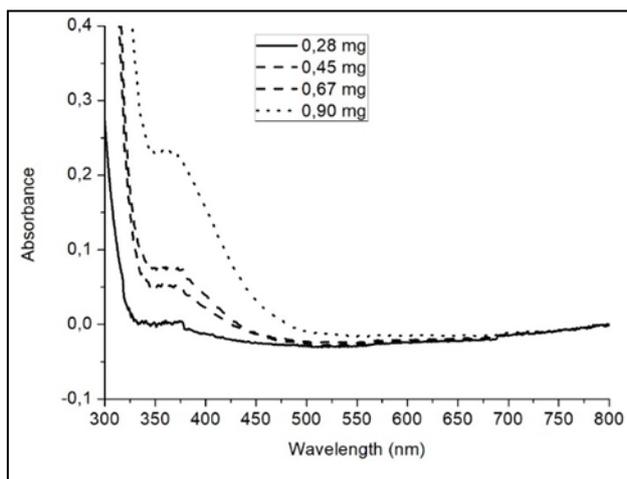


Figure 1. Absorption spectroscopy of the PEEL solution containing the  $\text{TiO}_2$  NP.

Although the DFT data also highlight the rather favourable interaction of the PEEL molecules with the oxidized silver surfaces, the oxidation of Ag is less likely to happen upon venting the sample, as compared to Ti. It was found that sputtered Ag atoms were not dispersed inside the PEEL solution.

Finally, Ag was sputtered over BMIMTFSI. According to [1,2], IL allows the production of metal nanoparticles through sputtering. No film formation on the surface of the ionic liquid was ever observed. On the other hand, one could observe with the naked eye a cloud of particles located underneath the surface of the liquid. This behaviour is like what was reported in [6]. These observations emphasize that the interaction between the IL surface and the sputtered metal atoms is different as compared to the situation encountered with PEEL. The presence of a high-concentration region under the surface can be explained by the fact that metal – IL molecule is rather efficient and promotes a relatively rapid incorporation of the silver atoms into the liquid, but their diffusion is slow due to the rather high viscosity of the IL (61.14 Cp). The nucleation and growth of the Ag-NP would therefore occur inside the solution. These IL-Ag solutions were analysed by UVS. An absorption peak appears at 410 nm (Fig. 2). But the absorption spectrum changes with time; the solution is not fully stable since the intensity of the peak at 410 nm decreases while another peak is found to increase in intensity at  $\sim 600$  nm (insert in Fig. 2). In [7] this of behaviour was attributed to NP agglomerating due to the presence of water inside the IL solution.

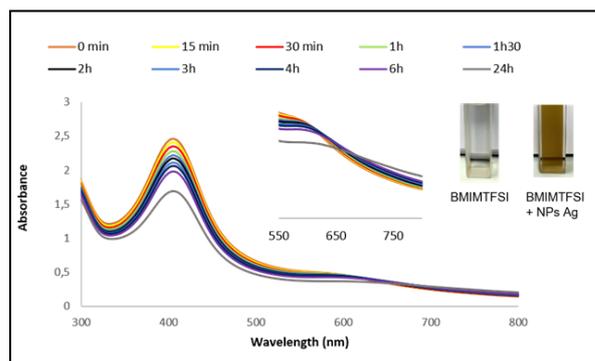


Figure 2. Absorption spectroscopy of the IL solution containing the Ag NP.

From the TEM analysis it is found that these Ag-NP are spherical and have a diameter ranging from  $\sim 5$  up to  $\sim 20$  nm. SAED analysis carried out on those samples highlight the presence of crystallized Ag-NP as well.

#### 4 Conclusions.

We studied the sputtering of Ti and Ag onto liquid substrates: PEEL, an OH-functionalized molecule, and an ionic liquid (BMIMTFSI). Depending on the nature of the metal and of the host liquid, the interaction of the sputtered atoms with the liquid surface is different. This obviously influences the growth mechanism of the nanoparticles and their physical properties.

#### 5 References

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