In-situ monitoring of nanoparticle formation in cluster source by UV-Vis spectroscopy

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Abstract: In-situ UV-Vis spectroscopy is a convenient and sensitive method for the monitoring of the metallic nanoparticle (such as Ag) formation in gas aggregation cluster sources. The effect of nanoparticle trapping in near-to-electrode region during the plasma existence was successfully detected. The discharge shutdown initiated the release of nanoparticles from the trapping region.

Keywords: nanoparticles, gas aggregation cluster source, in-situ UV-Vis spectroscopy.

1. Introduction

In the last decades, magnetron-based gas aggregation cluster sources (GAS) have been successfully applied for the fabrication of the variety of metal nanoparticles (NPs) [1]. Magnetron sputtering can be accompanied by the formation of NPs if the elevated pressure of a cold buffer gas is created in the vicinity of the target. Currently, the research is focused on the *ex-situ* characterization of NPs once they have been deposited onto substrates. The nucleation, growth and transport processes that occur inside the GAS are much more difficult for the investigation. Recently, *in-situ* small angle X-ray scattering (SAXS) was used for the detection of copper NPs and the measurements revealed the accumulation and trapping of the NPs in near-to-magnetron regions [2]. The existence of big (up to 100 nm) NPs in the trapping region was also unveiled, although they have never been previously observed by scanning electron microscopy (SEM) measured on the samples prepared outside the GAS Unfortunately, the overall concentration of NPs in the gas phase is low and reliable SAXS measurements require synchrotron radiation of high brilliance. In this work, UV-Vis spectroscopy was used for the in-flight detection of silver NPs inside the GAS by taking advantage of a particle plasmon resonance effect. UV-Vis spectroscopy is low-cost, fast and laboratory feasible technique. The aim of the research is to investigate whether *in-situ* UV-Vis spectroscopy may compete with SAXS in the agenda of the detection of plasmonic NPs.

2. Experimental part

Fig. 1 shows the scheme of the experimental equipment used for the in-situ SAXS measurements that has also been used for our experiments. A homemade GAS was constructed from a cylindrical water-cooled chamber with quartz windows for UV-Vis spectroscopy measurements. The chamber was equipped with a 81 mm movable magnetron with a silver target (Ag, purity 99.99 %) connected with DC power supply (MDX-500, Advanced Energy). The chamber was ended by a conical lid with a 1.9 mm exit orifice. The distance between the surface of the target and the orifice was set at 12 cm. The GAS was mounted onto a vacuum chamber in the vertical position. The whole system was pumped by scroll and turbomolecular pumps to the pressure of 2×10^{-4} Pa. The sputtering was carried out under the fixed parameters (the discharge current = 600 mA, the Ar flow = 18 sccm, the pressure in the GAS = 125 Pa). Optic fiber cables were connected with a light source and with a detector and were mounted on quartz windows. The UV-Vis spectra were recorded by a UV-Vis spectrometer (Ocean Optics USB2000+UV-VIS) in the range of 200 – 650 nm. The deposition rate of the NPs was controlled by quartz crystal microbalance (QCM) placed behind the orifice. Ag NPs were also characterized *ex-situ* by scanning electron microscopy (SEM) and transmittance electron microscopy (TEM).

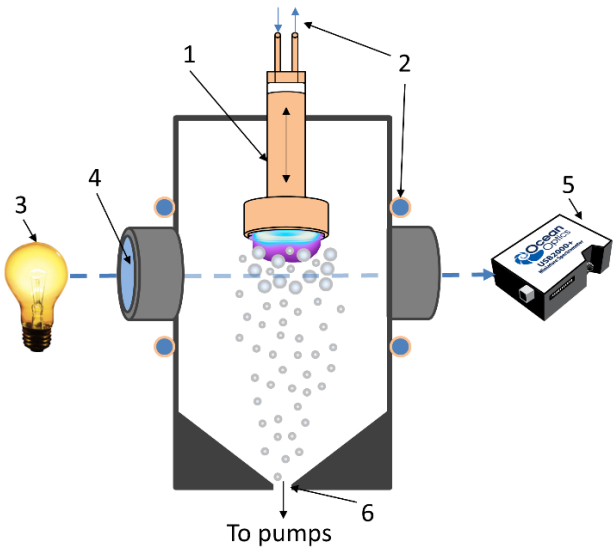

Fig. 1. Scheme of UV-Vis experiment: 1 – DC magnetron with Ag target; 2 – water cooling, 3 – light source, 4 – quartz window, 5 – UV-Vis spectrometer, 6 – orifice.

3. Results and discussion

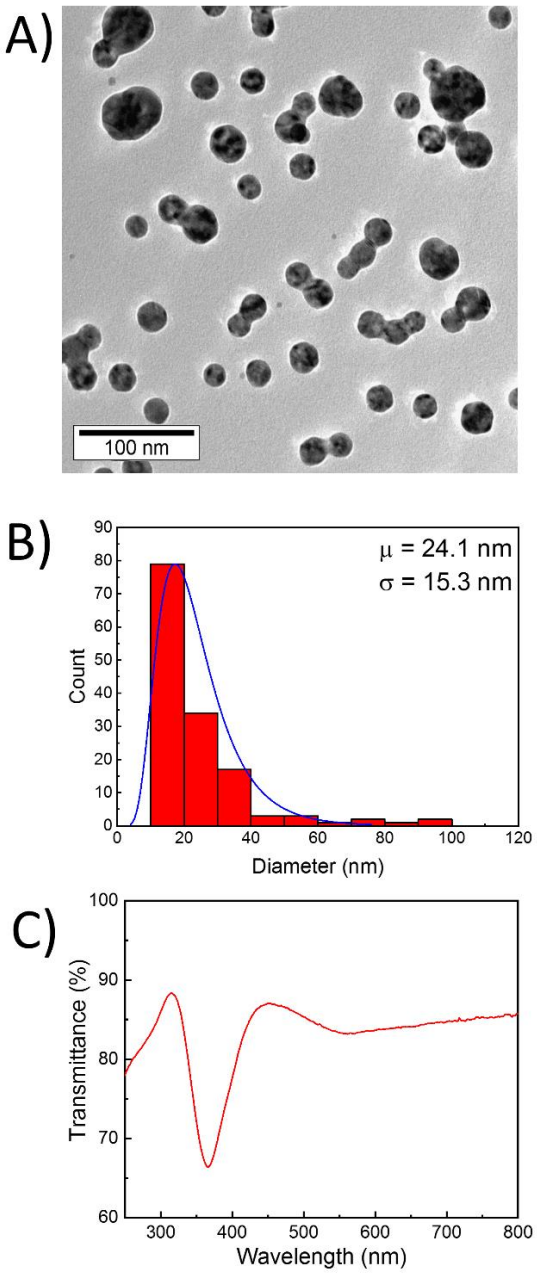

Fig. 2. *Ex-situ* characterization of Ag NPs: A) TEM image; B) size distribution (here μ – mean diameter; σ – standard deviation); C) UV-Vis spectrum.

Ag NPs produced under the chosen conditions have spherical shape and relatively broad size distribution. Fig. 2A and 2B demonstrate the TEM image of NPs and the corresponding size distribution histogram. The mean diameter of the NPs is 24 nm. The processing of the electron diffraction pattern confirmed the crystalline structure of the NPs. The NPs were deposited onto quartz substrates to determine the position of the plasmon peak (Fig. 2C). The sharp and intensive peak was found at the position of 365 nm, which is in good accordance with the values typically published for Ag NPs.

In-flight UV-Vis detection of the Ag NPs was first attempted behind the orifice (outside the cluster source). Fig. 3 shows the UV-Vis spectra measured during the GAS operation and after 1.5 seconds, when the discharge was shutdown. In the former case, the plasmon peak was found at 368 nm, which is in a good accordance with the results obtained *ex-situ*. However, the transmittance noticeably decreased after the discharge was switched off and the peak shifted toward the lower wavelength. This effect means that in a few seconds after the discharge shutdown the number of Ag NPs flown through the beam crucially increased. This effect may confirm the findings obtained previously by SAXS. A huge amount of Ag NPs was trapped in near-to-electrode region under the complex action of the electromagnetic and drag forces. In the moment when the discharge was switched off the equilibrium of the forces was violated and NP cloud was flown away with the gas flow.

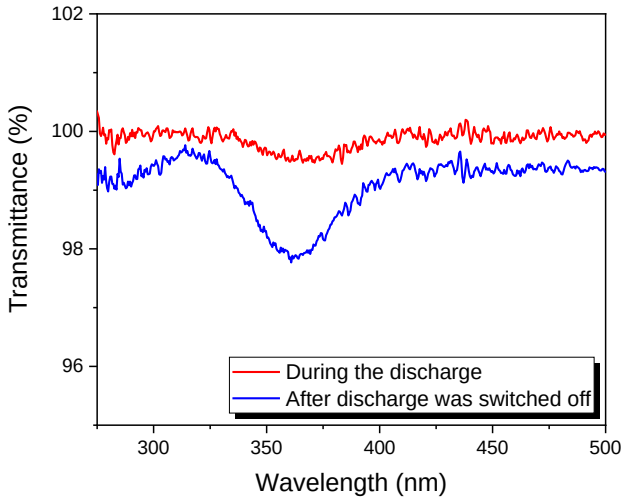

Fig. 3. UV-Vis spectra measured behind the GAS.

The UV-Vis measurements allowed also for the rough localization of the trapping region inside the GAS. Fig. 4 demonstrates the UV-Vis spectra measured along the GAS axis at different distances from the magnetron. At further distances, the plasmon peak looked identical to the one measured outside the GAS and it did not change. However, the intensity of the peak increased substantially if the light beam was moved very close to the magnetron. At the same time, at the distance 1.5 cm from magnetron to light beam the formation and intensification of Ag emission lines was observed in spectrum. It can be concluded, that Ag NPs are mostly trapped in plasma zone. This effect directly confirms the previous discovery of NP trapping in the near-to-magnetron region that was detected by SAXS. Thus, *in-situ* UV-Vis allows the detection of plasmonic NPs both outside and inside the aggregation chamber.

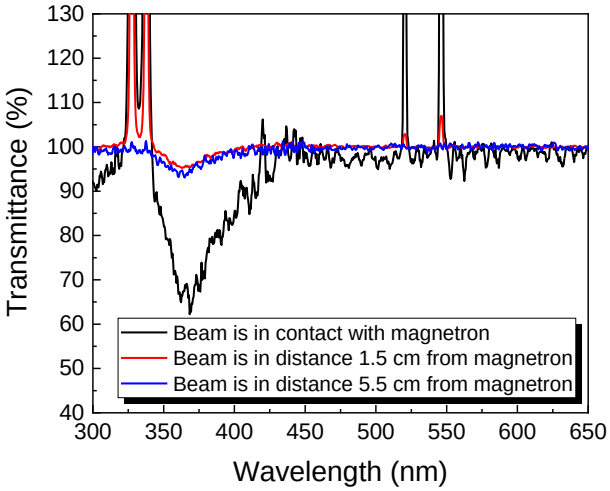

Fig. 4. UV-Vis spectra measured inside the GAS.

5. Conclusion

The plasmon peak corresponding to Ag NPs was successfully found in UV-Vis spectra both inside and outside the gas aggregation cluster source. The results confirmed the trapping of the NPs in the near-to-magnetron region found previously by SAXS. Thus, *in-situ* UV-Vis may prove to be a powerful method for the in-flight diagnostics of plasmonic NPs. The equipment is relatively cheap and the measurements are straightforward.

4. Acknowledgement

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5. References

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