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MASS SPECTROMETRIC INVESTIGATION OF SILVER CLUSTERS

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Abstract
Silver clusters were produced by two different synthesis procedures, related with different reduction species. PVA (polyvinyl alcohol) was successfully utilized as a source to reduce silver (Ag) metal ions without using any additional reducing agents to obtain Ag clusters. Silver clusters with atoms numbering 5-29 are registered through mass spectrometry using MALDI TOF and MALDI TOF/TOF techniques. Analysis showed that clusters with magic numbers are the largest, while those with an odd number of atoms are larger than clusters with an even number of atoms. Stability of these molecules, magic number actually, is in relation with their electronic configuration.

Introduction
For the first time some ten years ago, absorption spectra of silver clusters produced by different techniques in the 2.5–6.2 eV energy range were measured on clusters embedded in gas matrices or by gamma irradiation [1–3]. The spectra of small clusters (n < 12) are made of several narrow or broad peaks in the 3.0–4.5 eV range, while those of larger clusters are characterized by the emergence of a dominant and relatively broad peak between 3.2 and 3.8 eV. The position of this later was interpreted by the authors using a model based on the Mie theory in which the peak was described as the excitation of s-type electrons without direct contributions from d-type electrons. Nevertheless, the nature of the excitations needed to be confirmed by calculations in which the effect of d electrons would be taken explicitly into account. Hence, several theoretical *ab initio* studies have been investigated in order to reproduce the experimental spectra and to elucidate the real role played by the interband transitions associated to d-electrons. There are few experimental results, as we lack information about the stability and amplitude of different clusters as well as on ionisation energy.
The experimental mass spectrometry spectra of neutral, small and intermediate-size Ag_n (n=5-29) silver clusters produced by gamma irradiation, have been measured.

Materials and Methods
Silver clusters are created using radiolysis of the aqueous solution of $AgNO_3$ system, carbon nanotubes and PVA. Silver clusters and silver cluster decorated carbon nanotubes were created and have been further examined using mass

spectrometry methods. Reduction of silver ions was performed in the current of Ar or N_2O. The experiment showed that larger clusters were created and are more stable when radiolysis takes place in the current of N_2O. The irradiation was performed at a dose rate of 10 kGy/h up to the absorbed dose of 55 kGy. MALDI TOF and MALDI TOF/TOF techniques were used to analyze produced silver clusters.
An aliquot of each sample solutions containing an internal standard was combined 1:1, with the CHCA matrix and mixed thoroughly. Aliquots (0.50 µL) of the mixtures were spotted onto a 100-spot sample plate (Applied Biosystems) and air-dried. Mass analysis was performed in the positive ion reflector mode using a 200 Hz frequency pulsed N_2 laser operating at 337 nm. Five spectra at each of 10 randomly selected positions were accumulated per spot between 170 and 500 g/mol using the MS positive ion reflector mode acquisition method. Calibration of the instrument was realized using Calibration mixture 2 as the external standard. To generate spectra with high mass accuracy, an internal calibration was performed. For the analysis of silver clusters, 1.0 mg/mL solutions in 0.10 % trifluoracetic acid were prepared. Positive-ion MALDI-TOF and MALDI-TOF/TOF mass spectra were performed using the 4700 Proteomics Analyzer (Applied Biosystems).

Results and Discussion

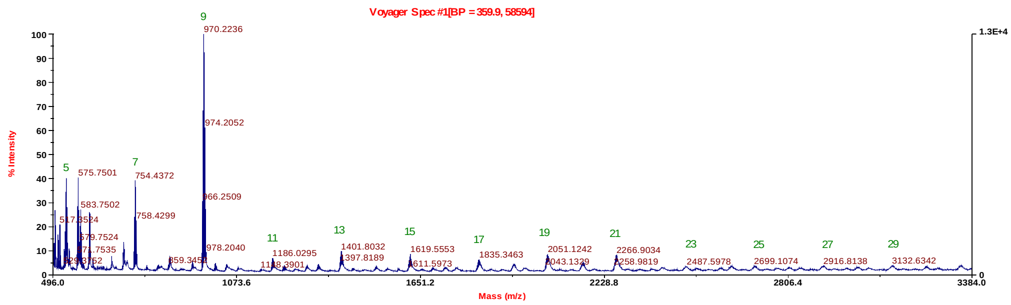

Fig.1. MALDI TOF spectrum of silver clusters. Numbers above the mass values (5 to 29) show the number of silver atoms in the clusters.

Silver clusters with the number of atoms from 5 to 21 showed satisfactory stability. Only clusters with 11 atoms of silver appeared to be unstable, and decomposed in the time of flight reflectronic way. Fragments which were produced during this process, were cationized with Na positive single ions. The ancestry of these ions is unknown, and it may be speculated that these have appeared out of a cluster forming system. MALDI TOF spectrum of the obtained positive cluster ions is shown on Figure 1.

Conclusion

Our novel method of silver cluster formation from silver salts is reproductive and very simple. Clusters with the number of atoms from 5 to 29 were registered by mass spectrometry, where silver clusters with the number of atoms from 5 to 21 showed satisfactory stability. The literature predicted the matching magic numbers which are in relation with the electronic configuration of the cluster. Evidently, the most stable clusters are those with closed electron shells.

The results obtained from MS/MS analysis of the different clusters clearly demonstrate that MALDI-TOF/TOF can be used to discriminate unstable silver clusters with good reproducibility.

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