

Uptake of Ag nanoparticles into plant roots – specific problems in EXAFS analysis

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In the increasing production and use of engineered nanomaterials silver nanoparticles (Ag NP) are among most used due to their antibacterial properties. With a steady release into the environment, animal and human health may be at risk. In a study of Ag transport in environment, mechanisms of plant root uptake of AgNPs and Ag speciation in plants is investigated by X-ray absorption spectroscopy (XAS).

The lettuce (*Lactuca sativa*) plants were grown hydroponically in Hoagland nutrient solution supplemented with 3, 5 and 10 mg/L of AgNPs with different surface coatings (citrate, PVP and PEG). The roots were homogenized and prepared as frozen-hydrated and freeze-dried samples for the measurements at the ALBA synchrotron, Barcelona, Spain. Utilizing He cryostat and CdTe detector at the Claess beamline Ag K-edge EXAFS spectra were measured in fluorescence mode with a total collection time of ~2 hours in consecutive runs, to ensure the useful interval up to $k = 10 \text{ \AA}^{-1}$. IFEFFIT code [1] was used in the analysis of data.

The prevailing feature in EXAFS spectra of all samples is the signal of the neighbor Ag atoms in the nanoparticle, following the spectral features of bulk Ag metal up to 5 Å. The contribution of low-Z organic ligands is hardly noticeable beneath the signal of ~12 strongly scattering Ag neighbors. Two candidate ligands are identified in preliminary survey: sulfur at 2.35 Å, and oxygen at 2.05 Å.

In the Feff model constructed from the first 5 scattering paths of Ag metal lattice and single paths of O and S ligands, the number of required parameters is at par with the number of freedom degrees of the usable part of the spectrum. Statistically stable values of the parameters can thus only be gained in collective fitting, preferably of groups of spectra of related samples, so that common values can be assumed for some parameters. When parameter values for a given sample from fitting in different groups are compared, their reliability can be assessed. Those pertaining to the NP neighborhood are highly reliable, with the spread in the percent range. The parameters of the S-shell vary typically for 25 %, and those of O-shell more than 50%.

A direct insight into the mechanism of Ag uptake in the root is connected to the coordination numbers of the ligands and their normalization: can the large spread of the fitted values of S and O be cured by a restraint that an Ag atom be either part of an NP with 12 nominal Ag neighbors, or attached to an O or S? It can, somewhat, only with an effective NP coordination below 12 Ag. Then, the coordination of S shows that up to 40% of Ag atoms are involved in a thio- bond: a strong indication that Ag is effectively eluted from the NP. The issue of O ligands is less clear: it concerns the question how the coating adheres to the NP body and how the NP is attached to the root cell wall.

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