Time, pH, and size dependency of Ag^+ release in relation to the surface structure of silver nanoparticles

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Toxicity of silver nanoparticles (AgNP) has been related to the release of ionic silver. This process is influenced by a large variety of factors and is poorly understood. Key for understanding Ag^+ release from AgNP is subvalency. Subvalency is a fundamental property of Ag that can be elucidated for a specific class of materials with a bond valence analysis of crystal structures [1]. Subvalency of Ag will be evaluated for Ag materials as well as for the structure of a AgNP precursor, i.e. $Ag_{13}(OH)_4$, that has been optimized with MO/DFT (molecular orbital/density functional theory).

The surfaces of AgNP in an oxidative environment are covered by semi-metallic silver. At the 111 faces, Ag has a subvalency of +⅓ v.u. giving rise to the presence of $\equiv Ag_3OH$ surface groups [1]. Pristine AgNPs may release Ag^+ ions by the oxidative dissolution of these groups via different pathways. In the present study, we quantify the time, pH, and size dependency of the silver ion release from AgNPs and explain our results in a consistent manner with a mechanistic view that we have developed.

Undersaturation of a solution, created by acidification, will initiate a fast oxidative dissolution process in which a pristine AgNP surface can be opened at particular points that grow laterally until a full layer of Ag is stripped off while, at the newly exposed surface, $\equiv Ag_3OH$ is reformed. This irreversible process ends if the undersaturation of the solution is sufficiently diminished by the Ag^+ release during ~ 1 day [2].

The initial AgNP surface with $\equiv Ag_3OH$ can also release Ag^+ via a second pathway in which oxidative dissolution simultaneously leads to the formation of a new structural surface state [2]. This process dominates at circum-neutral pH conditions. Equilibrium between the initial and new surface state can be described well with a formulated thermodynamic model. The equilibrium constant ($\log K$) is found to be linearly related to the specific surface area of AgNPs of different size. This particle size dependency of $\log K$ can be explained by a surface Gibbs free energy contribution. Analysis of the kinetic release of Ag^+ suggests a rate limitation by either adsorbed molecular O_2 or by the H^+ concentration in solution.

References

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