On the Mechanisms of Formation of M^0-nanoparticles via the Reduction of M^nL_m Complexes

Alina Sermiagin[1], Totan Mondal[1], Dan Meyerstein[1,2], Ronen Bar-Ziv[3], Haya Kornweitz[1], Tomer Zidki[1]

[1] Department of Chemical Sciences, The Radical Research Center and the Schlesinger Family Center for Compact Accelerators, Radiation Sources and Application, Ariel University, ΔΔΔ Ariel, Israel

[2] Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva, Israel

[3] Department of Chemistry, Nuclear Research Centre Negev, Beer-Sheva, Israel

It is commonly suggested that the mechanism of formation of M^0-nanoparticles, M^0-NPs, via the reduction of M^nL_m complexes, including $M(H_2O)_m^{n+}$ proceeds via the following scheme:

I. I. M^nL_m + reducing agent → M^0 + mL + oxidized reducing agent

II. $kM^0 \rightarrow M_k^0 \rightarrow \rightarrow M^0$-NP

However, the redox potentials of most reducing agents used do not enable the reduction of M^nL_m to M^0_{atoms}. This is due to the following: The redox potential of the couple $M(H_2O)_m^{n+}/M^0_{(s)}$ can be calculated from the following equation:

$E^0(M(H_2O)_m^{n+}/M^0_{(s)}) = (\Delta G0evaporation + \Delta G0ionization + \Delta G0hydration/solvation)/nF$

Clearly if one wants to calculate the redox potential of an atom no evaporation is involved and therefore $\Delta G^0_{evaporation}$ is not contributing. Therefore, the redox potentials of atoms are:

$E^0(M(H_2O)_m^{n+}/M^0_{(atom)}) = E^0(M(H_2O)_m^{n+}/M^0_{(s)}) - (\Delta G^0_{evaporation}/nF)$

As a result most $E^0(M(H_2O)_m^{n+}/M^0_{(atom)})$ are very negative and the mechanism of formation of M^0-NPs does not involve the formation of M^0_{atoms}.

The mechanisms of formation of Ag^0-NPs via the reduction of $Ag(H_2O)_2^+$ by H_2 and by BH_4^- will be discussed in detail.