The impact of the electron dose rate and temperature-dependent radiolysis products on the growth and dissolution of metal nanoparticles in LTEM

Šturm, S.[1], Prasnikar, A.[2], Hodnik, N.[2], Likozar, B.[2], Zuzek Rozman, K.[1], Kostevsek, N.[1] and Ambrozic, B.[1]

[1] Jozef Stefan Institute, Slovenia, [2] National Institute of Chemistry, Slovenia

Significant advances in the development of novel functional nanomaterials can be achieved by using suitable microscopy methods that allow investigations on nanoparticles in their native environments at high spatial and temporal resolution, which is achieved by applying transmission electron microscopy (TEM) combined with the specialized liquid cells (LTEM). This ground-braking approach opens wide range of possibilities where case-by-case specialized experiments can be performed by proper redesign of liquid chambers, allowing to perform direct nucleation and growth experiments of nanoparticles either from solutions at elevated temperatures or during the electrodeposition, at the nanoscale and in real time.

Although LTEM has a great potential, it also poses some great challenges that need to be properly assessed in order to justifiably correlate LTEM experiments with the tabletop-scale experiments. This is mainly related to the relatively constrained space in the liquid cell, direct interaction between the electron beam and the sample, and the effect of the water radiolysis. In relation to this, it was already reported in the previous studies that the nucleation and early growth pathways of nanoparticles from aqueous solutions can be significantly altered as a consequence of water radiolysis, which is inevitable during the LTEM experiments [1]. This is mainly due to the formation of various radicals, implying that the system in the LTEM cannot be freely observed without affecting it. For example, solvated electrons, e_h^-, and hydrogen radical, $H^\bullet$, are strong reducing agents, which can provoke metal precipitation, while some radiolytic species are strong oxidative agents causing metal dissolution, like hydroxyl radical ($OH^\bullet$). Only by establishment of the precise quantitative model for radiolysis the experimental results can be put in the proper context, for example, by including the radiolysis products in the whole experimental reaction sequence.

In this study we present an improved radiolysis model based on the initial model developed by Schneider, N.M. *et al.* [2], which allows more comprehensive interpretation of the LCTEM experiments related to the metal nanoparticles growth and dissolution phenomena in aqueous solution during the LTEM experiments. The improved radiolysis model, beside the electron dose rates additionally includes the effect of temperature between 20°C and 100°C., pH and the formation of gaseous phases in the aqueous solution. Based on the calculated dynamic equilibrium of the overall oxidative and reductive radiolysis species and consequent oxidising/reductive power of radiolysis products for the various metallic systems, the nucleation and dissolution regions as a function of electron dose rates and temperature can be established and correlated with the experimental results. Finally, to validate the improved radiolysis model we have performed detailed in situ LTEM studies on model system, gold nanoparticles nucleation, early growth and dissolution phenomena from aqueous solution at varying experimental conditions. The obtained radiolysis model suggests that the metal precipitation and dissolution regions are strongly influenced by the combined effect of the initial pH value and temperature of the solution together with the electron dose rate used during the experiments (Figure 1).

References:

[1] Ross, F.M., 2015. Opportunities and challenges in liquid cell electron microscopy. *Science*, *350*(6267), p.aaa9886.

[2] Schneider, N.M., Norton, M.M., Mendel, B.J., Grogan, J.M., Ross, F.M. and Bau, H.H., 2014. Electron - water interactions and implications for liquid cell electron microscopy. *The Journal of Physical Chemistry C*, *118*(38), pp.22373-22382.

[3] This work was supported by the Slovenian Research Agency and Jožef Stefan International Postgraduate School (IPS).

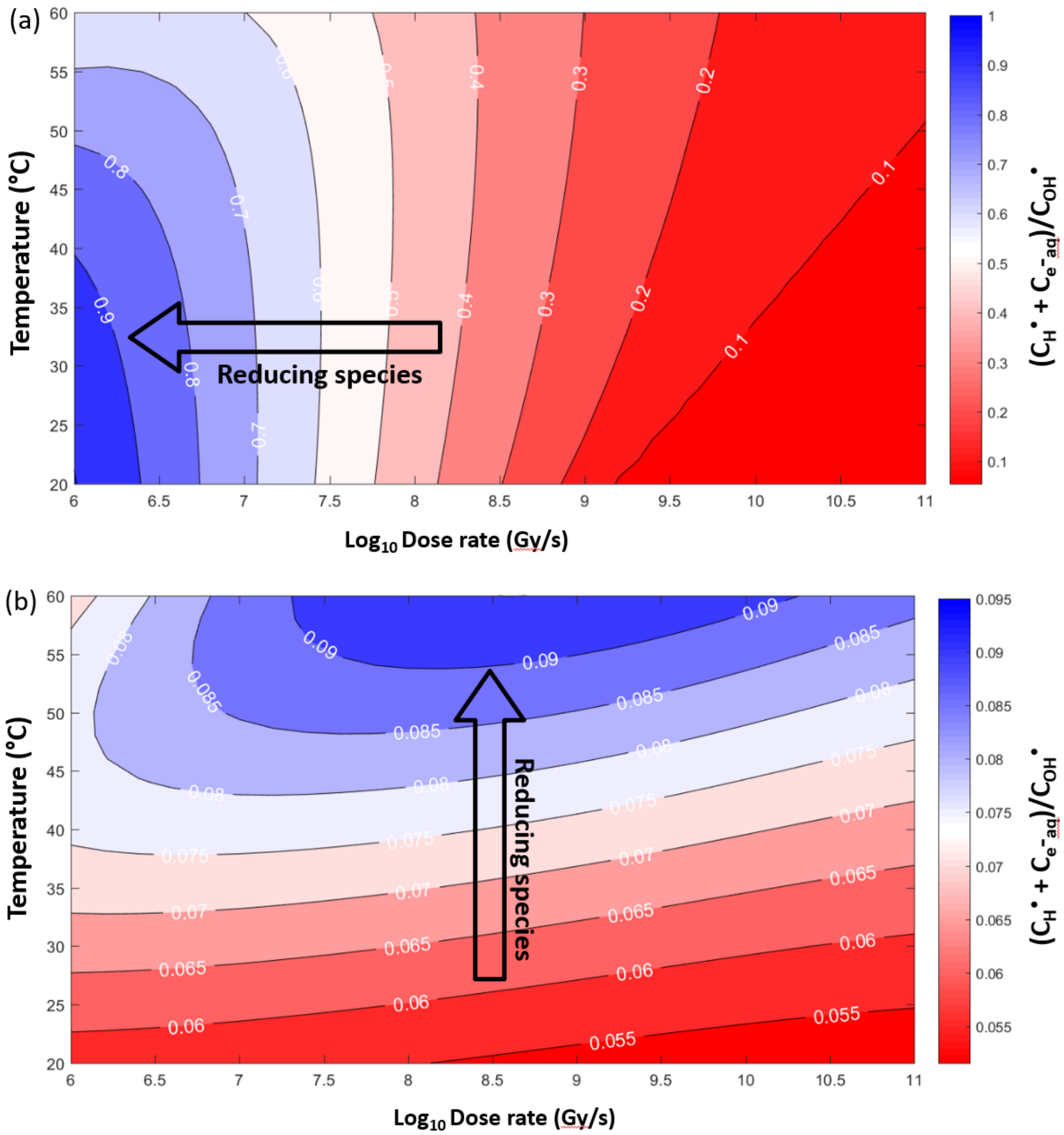

Figure 1 Simulation of water radiolysis in LTEM: Ratio of equilibrium concentrations of the most reducing and oxidizing species at varying initial pH value of the aqueous solution; (a) pH=2.8 and (b) pH=7.