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Modelling the Radiolysis of Silver Nitrate Solutions in presence of Bromide Ions in Liquid-Phase Transmission Electron Microscopy

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In this study, we model the radiolysis chemistry of aerated $AgNO_3$ solutions during liquid-phase transmission electron microscopy (LP-TEM) in presence of bromide ions using a Python-based adaption of the radiolysis model of Schneider *et al.* [1]. We verify the model qualitatively by comparing the results with experiments using a graphene-supported microwell liquid cell [2,3]. LP-TEM is a powerful, yet novel method for analyzing dynamic processes of nanostructures in liquid environment. One of the major challenges for enabling LP-TEM to become a standard characterization method, however, is the development of accurate physical models describing electron-beam interactions with liquid specimen, e.g. heating [4], radiolysis [1,2,5,6], and charging effects [7]. In particular, the model of Schneider *et al.* [1] describing radiolysis of deionized and deaerated water under electron beam irradiation has been used intensively to explain a vast variety of LP-TEM-specific phenomena.

Recently, complex particle growth and dissolution studies investigating gold-silver heterostructures obtained high interest in research [2,8]. In order to support the proposed interpretation of experimental results, we elaborate an adaption of Schneider's radiolysis script to describe the reaction chemistry of aerated $AgNO_3$ solutions in presence of bromide ions, which originate from stabilizing agents like cetrimonium bromide (CTAB). Besides water, this requires 36 additional species and yields a reaction set comprising 232 coupled ordinary differential equations. The original Matlab©-based script is ported to open source software (Python) as a first step towards an easily accessible simulation program. We find excellent agreement in both performance and outcome of our script with the initial version. A validation of our model is achieved by comparison with LP-TEM experiments on silver-shell growth on gold nanorods using an in-house developed liquid-cell architecture [2,3] in combination with a Philips CM-30 (S)TEM operated at 300 kV and electron flux densities between 10^4 and 10^5 $e^-nm^{-2}s^{-1}$.

Figure 1a shows the outcome of the simulated model describing the evolution of concentrations of reactants at different $AgNO_3$ concentrations (10^{-2} M: solid lines; 10^{-3} M: dashed lines). A comparison of both simulated concentrations reveals main differences for an excess of Ag^+, suggesting an equilibrium balance between precipitated AgBr and Ag^+ ions required for formation of elementary silver (black data). The concentration of AgBr (blue data) remains nearly constant at an excess of Ag^+ (10^{-2} M) in contrast to the low concentration (10^{-3} M) where it drops by more than 50%. Figure 1b shows the dependency of steady state concentrations on the dose rate for different silver species. Previous LP-TEM experiments at high dose rates presented by Hutzler *et al.* [2] revealed underpotential deposition of silver shells on Au nanorods. This observation correlates with the layer-by-layer dissolution of AgBr nanocrystals, controlled by the electron flux density via distinctly generated radiolytic species. These findings are in good agreement with the decrease of steady state concentrations of Ag^+ (Fig. 1b, red data) due to a reduction to

Ag (black data) on the surface of gold nanorods. This is counterintuitive due to AgBr being highly sensitive to radiation. A disruption of the solution equilibrium of AgBr and its solvated ion pair (Fig. 1a, Br^-: green data and Ag^+: red data) for low Ag^+ concentrations and the presence of high concentrations of hydroxide radicals (which are able to compensate free charge carriers in AgBr) are assumed to be the driving force for this anomalous behavior. Only at high dose rates, layer-by-layer dissolution of AgBr is observed, which supports this hypothesis. At low dose rates, in turn, the expected growth of silver nanoparticles by direct reduction of AgBr is observable.

In summary, we present a comprehensive kinetic model for simulating radiolysis of aqueous solutions containing $AgNO_3$ and bromide ions. The outcomes are in good agreement with experimental data. It is, thus, a useful tool for further investigations of the chemical and physical observations happening during LP-TEM.

[1] N M Schneider *et al*, J. Phys. Chem. C **118** (2014), p. 22373.
[2] A Hutzler *et al*, Nano Lett. **18** (2018), p. 7222.
[3] A Hutzler *et al*, J. Vis. Exp. (2019), Art. No. e59751.
[4] B Fritsch *et al*, Nanoscale Adv. **3** (2021), p. 2466.
[5] J M Grogan *et al*, Nano Lett. **14** (2014), p. 359.
[6] A Hutzler *et al*, Adv. Mater Interfaces **6** (2019), Art. No. 1901027.
[7] P Liu *et al*, Nano Lett. **20** (2020), p. 1944.
[8] K Aliyah *et al*, J. Phys. Chem. Lett. **11** (2020), p. 2830.
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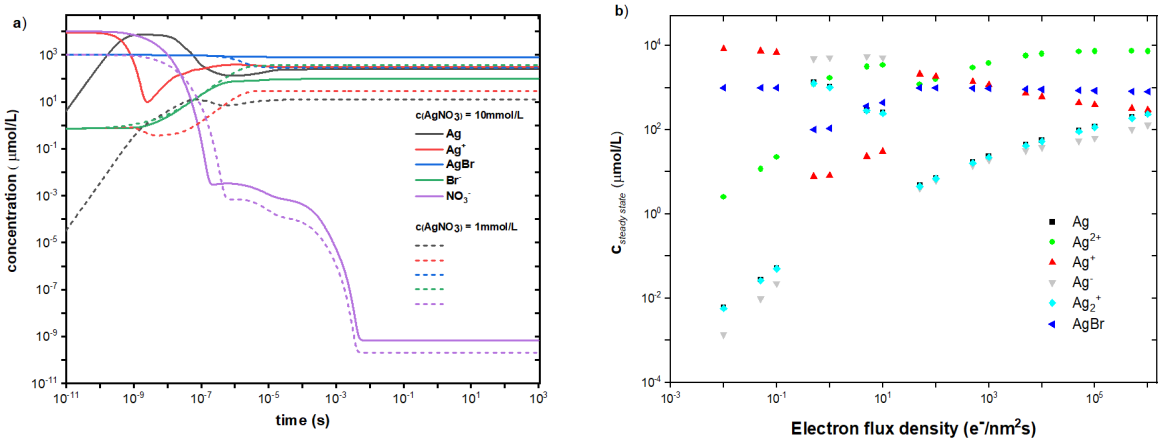

Figure 1. Simulation results of (a) the evolution of the concentration of distinct species emerging during LP-TEM for $AgNO_3$ (10^{-2} M: solid lines; 10^{-3} M: dashed lines) and Br^- containing solutions (CTAB, c = 10^{-3} M) at the electron flux density of 10^5 $e^-nm^{-2}s^{-1}$ and (b) dependency of the steady state concentrations of relevant silver species on the electron flux density.

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