

Nanoparticle formation mechanisms and molecular intermediates revealed by liquid phase EM and reaction pathway analysis

Ms. Jiayue Sun¹, Mr. Birk Fritsch², Mr. Andreas Körner², Ms. Lucia Morales², Mr. Chiwoo Park³, Ms. Mei Wang⁴, **Dr. Andreas Hutzler²**, Mr. Taylor Woehl⁴

¹Department of Chemistry and Biochemistry, University of Maryland, College Park, United States, ²Helmholtz Institute Erlangen-Nürnberg for Renewable Energy, Erlangen, Germany, ³Department of Industrial and Systems Engineering, University of Washington, Seattle, United States, ⁴Department of Chemical Engineering, University of Maryland, College Park, United States

Classical nucleation theory (CNT) is used to describe the growth of metal nanoparticles by seed formation from insoluble metal atoms generated by chemical reduction of precursors containing metal ions. It involves a nucleation step, and subsequent monomer attachment on the seeds which is limited by diffusion of metal atoms.

In contrast, liquid phase transmission electron microscopy (LPTEM) has revealed that nanoparticles do not form by the above-mentioned process but via cluster-cluster aggregation instead.[1] Although this non-classical growth of nanoparticles has been observed frequently, precise knowledge about atomic and cluster species remains concealed. Mechanisms comprising thermodynamically preferred cluster sizes have been suggested in prior studies. However, these magic clusters cannot explain formation mechanisms involving strong reductants at room temperature where kinetics are dominated by the reaction.

In LPTEM, reaction kinetic modeling has been shown to facilitate uncovering reaction conditions in irradiated solutions and how to tailor redox chemistry [2] and acidity [3] in precursor solutions with radiation.

Unraveling ionic precursor species guiding the formation pathways of metallic nanoparticles would enable to specifically design synthesis routes and thus to deliberately adjust their nanostructure properties.

Herein we correlate liquid phase electron microscopy with reaction throughput analysis to demonstrate that nucleation and growth of silver nanoparticles is based on aggregation and attachment of various metal clusters and ions. Therefore, we utilize LPTEM to study nucleation and growth rate of silver nanoparticles induced by radiolysis of aqueous silver nitrate solution. [4] Observations are complemented by a time dependent radiolysis model of the precursor solution (Figure 1a and 1b) illustrating the concentration of most silver species being directly proportional to electron dose rate (Figure 1c).

LPTEM measurements revealed a nearly invariant nanoparticle growth rate with increasing electron dose rate and a decreasing nucleation rate (Figure 1d and 1e). Furthermore, our reaction kinetic model suggests that Ag₄ and Ag⁻ have steady state concentrations orders of magnitude larger than those of the other species which are also almost invariant with dose rate. Experimental dose rate dependent growth and nucleation rates were fitted by power laws yielding growth exponents of $(2.5 \pm 7.5) \cdot 10^{-2}$ and -0.17 ± 0.07 , respectively (Figure 1d and e, red lines). The large concentrations of Ag₄ and Ag⁻ in combination with their dose rate dependent power law exponents of $(-7.5 \pm 1.0) \cdot 10^{-3}$ and $(6.5 \pm 2.6) \cdot 10^{-3}$ indicated by our kinetic model and located within the error margin of the experimentally obtained data, suggest a nanoparticle growth by attachment of Ag₄ and Ag⁻ to the silver seeds. However, the nucleation rate exponent did not match any of the simulation results. Furthermore, CNT

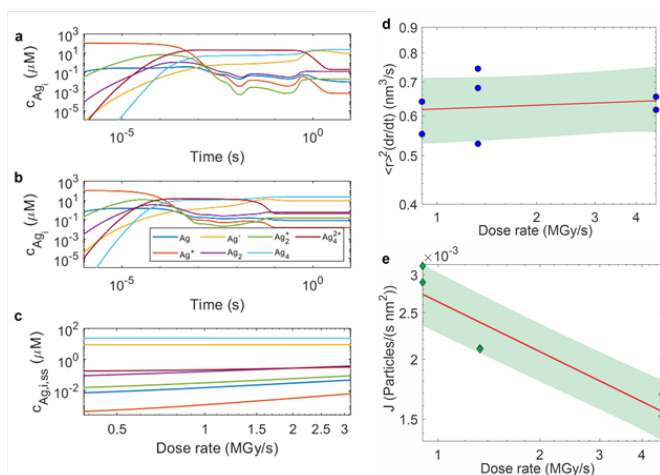
evaluation yields very high supersaturation values suggesting unrealistically small critical radii of no more than a single atom.

The inconsistency of the dose rate dependency of the observed nucleation rate with that of all silver species and CNT suggests a silver nanoparticle growth via a non-classical pathway. Our results provide evidence, that nucleation rather takes place in a millisecond time scale which is dominated by Ag_4^{2+} cluster-cluster aggregation. Overall, this work showcases the power of quantitative LPTM combined with transient reaction kinetic modeling for disentangling which chemical processes are involved in nanoparticle formation.

Figure caption

Figure 1. (a) and (b) Radiolysis model for a dose rate of 0.56 MGy/s and 5.6 MGy/s. (c) Steady state concentration of silver species as a function of dose rate. (d) Growth rate multiplied by the squared particle size as a function of dose rate. The blue symbols represent experimental measurements. The red line is a fit assuming diffusion limited growth to the Lifshitz-Slyozov-Wagner (LSW) model. (e) Nucleation rate as a function of the dose rate fitted by a power law. Green symbols are experimental nucleation rates and the red line a power law fit. The green shaded region represents the 3σ confidence interval for the fits.

Graphic:



Keywords:

LPTM; nucleation; growth; silver; nanoparticles

Reference:

- [1] J. De Yoreo et al., Science 349, 2015, aaa6760, DOI: 10.1126/science.aaa6760
- [2] B. Fritsch et al., Adv. Sci. 9, 2022, 2202803, DOI: 10.1002/adv.202202803
- [3] B. Fritsch et al., J. Phys. Chem. Lett. 14, 2023, 4644–4651, DOI: 10.1021/acs.jpcclett.3c00593
- [4] M. Wang, C. Park, T. J. Woehl, Chem. Mater. 30, 2018, 7727, DOI: 10.1021/acs.chemmater.8b03050