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

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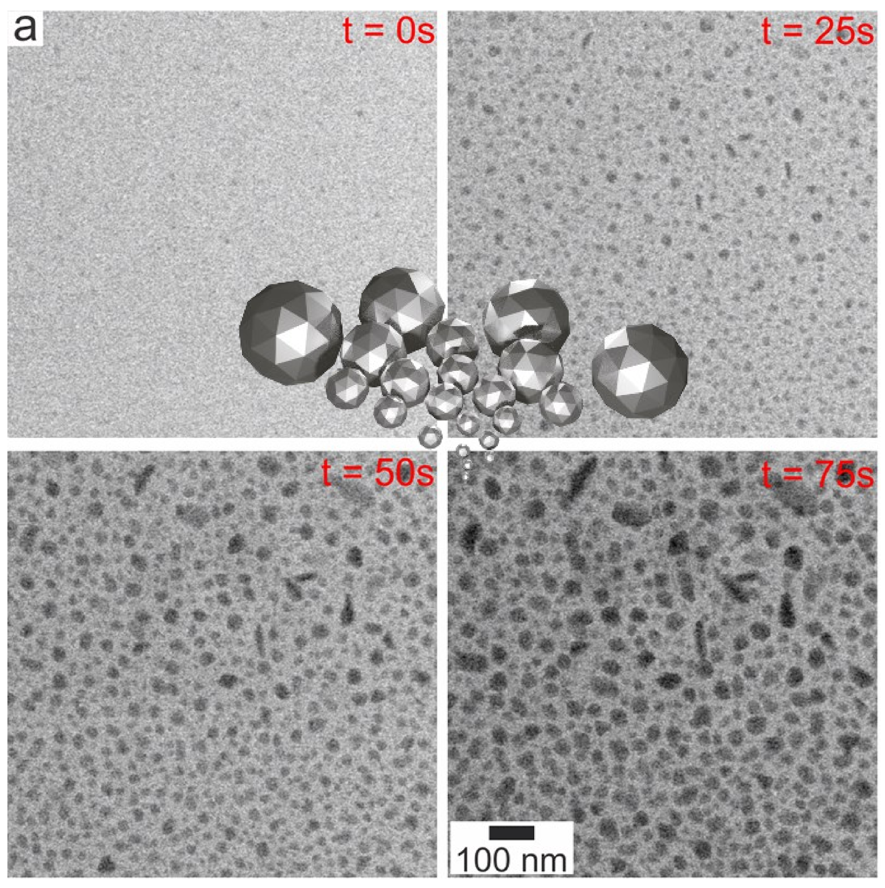
In situ electron beam driven Ag NP formation
Mechanisms and Intermediates?

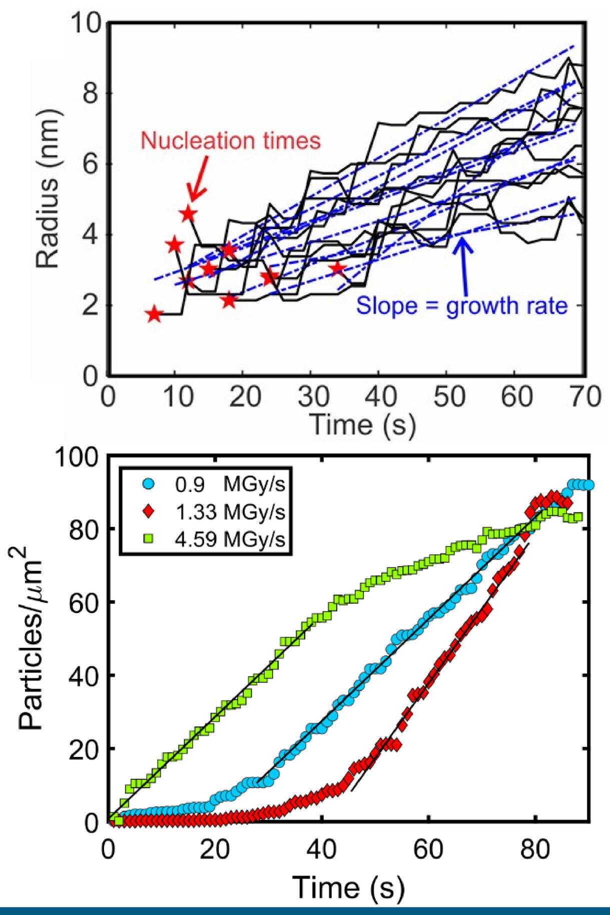
- JEOL JEM-2100F @ 200 kV
- BF-STEM, 5 µs, 100 kx
- Dose rate varied via spot size
- Protochips Poseidon Select
- 0.1 mM $AgNO_3$ + 0.1 M *t*-BuOH (OH radical scavenger)

[1] Ag growth: $Ag^+ + e_h^- \rightarrow Ag$; $Ag^+ + H^\bullet \rightarrow Ag + H^+$

Ag etching: $OH^\bullet + HO_2^- \rightarrow H_2O + O_2$; $Ag + O_2 \rightarrow Ag^+ + O_2^-$

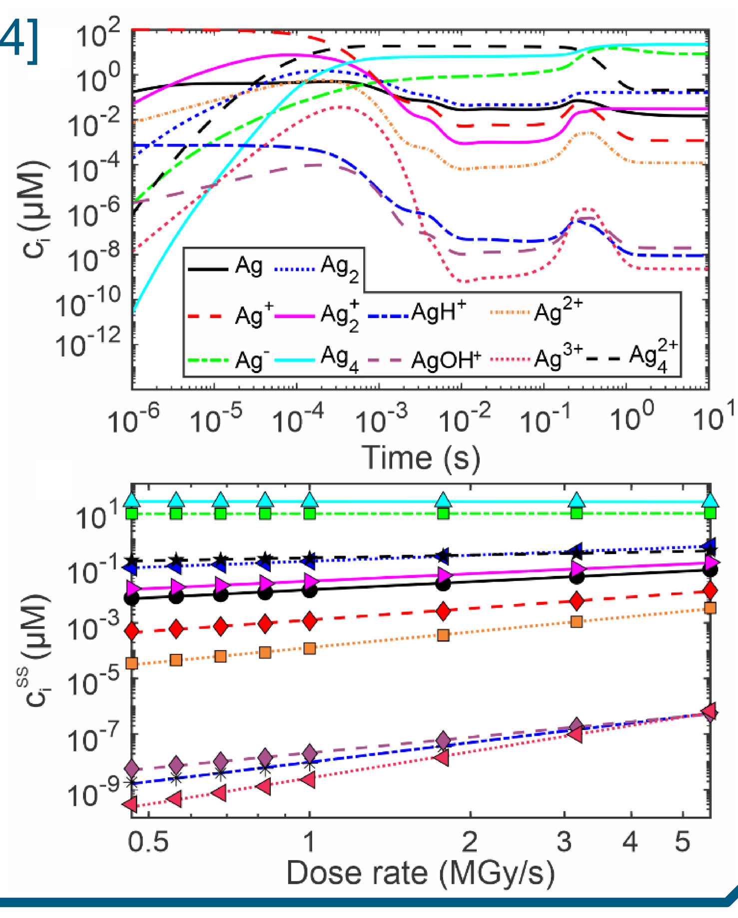
[2]





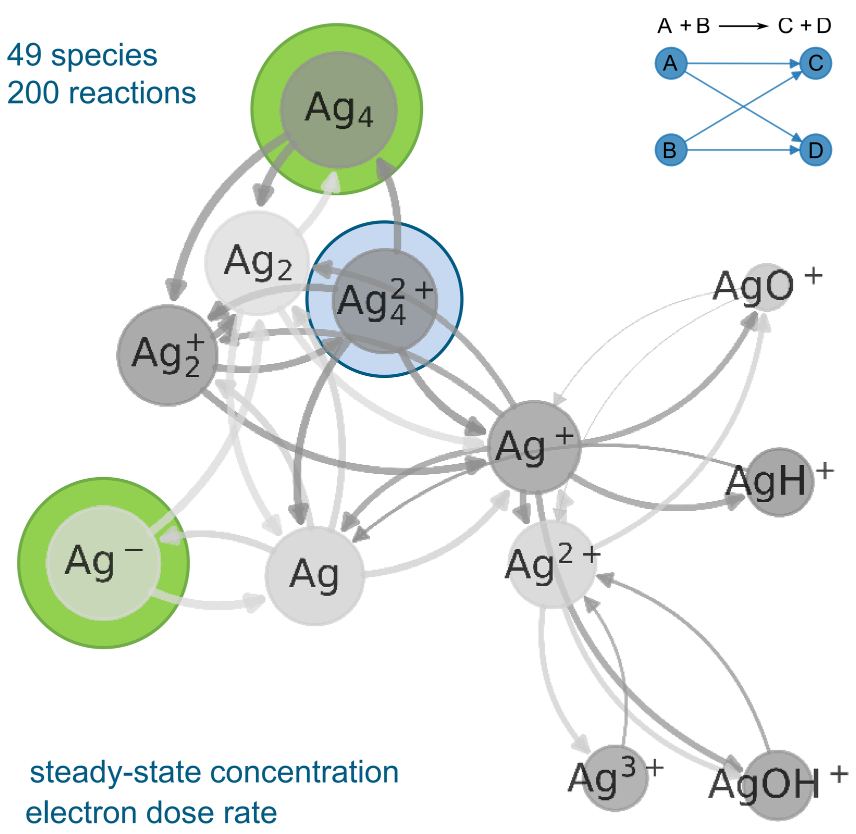
Can we describe this with kinetic modeling[3]?

[4]



Radiolysis modeling

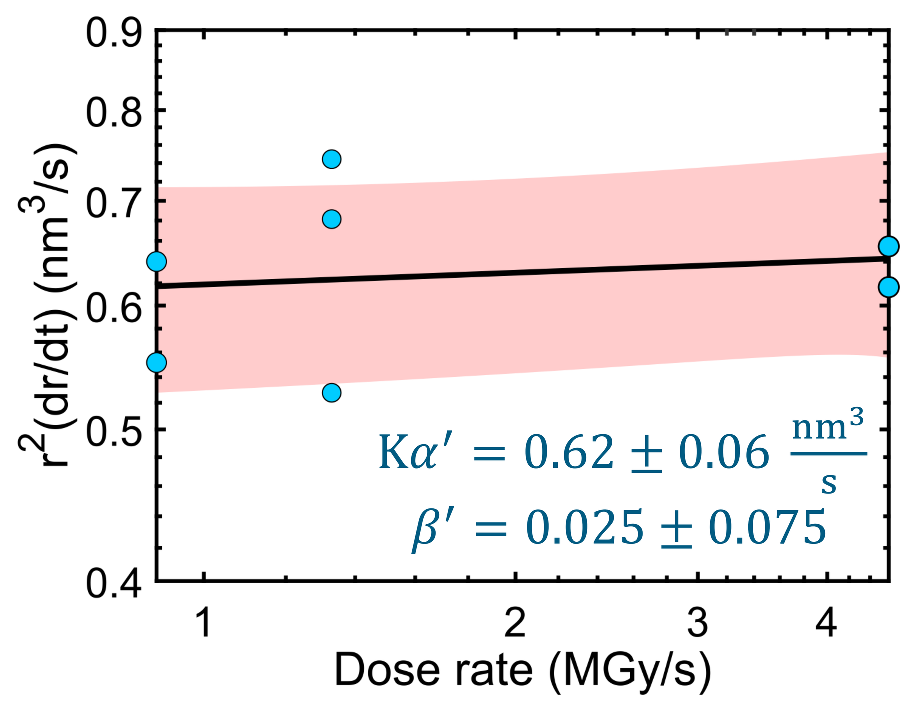
with **Auto**mated **Ra**diation **Ch**emistry [3]



c_i^{ss}: steady-state concentration
$\dot{d}$: electron dose rate
α_i, β_i: fitting parameter

Power-law-dependent steady states [5]: $c_i^{ss}(\dot{d}) = \alpha_i \dot{d}^{\beta_i}$

Diffusion limited growth



$K\alpha' = 0.62 \pm 0.06\ \frac{nm^3}{s}$

$\beta' = 0.025 \pm 0.075$

Growth described by Ag^- and Ag_4

$\frac{dr}{dt} r^2 = K\alpha' \dot{d}^{\beta'}$

Ag NP growth modeling

Lifshitz-**S**lyozov-**W**agner (LSW) model

For diffusion limited growth ($k_d \gg D$)

$$\frac{dr}{dt} \approx Kcr^{-2}$$

$$K = \frac{2\sigma D V_m^2}{RT}\left(\frac{r}{r_b} - 1\right), \quad \left(\frac{r}{r_b} - 1\right) \approx 1$$

$$D \approx 10^{-12}\ \frac{m^2}{s}$$

$$\sigma \approx 1\ \frac{J}{m^2}$$

r: particle radius
t: time
σ: surface energy
V_m: molar volume
c: precursor concentration
r_b: critical radius
R: universal gas constant
T: temperature
D: diffusion coefficient
k_d: surface attachment rate

Ag NP nucleation modeling

Classical **N**ucleation **T**heory (CNT) model

X Inconsistent with experimental data

- Fitted Ag solubility too large
  c_0: 10^{-5} – 10^{-6} M → 10^{-12} M expected
- Estimated critical radius too small r_b: 1 Å
  → main assumption (crystalline nuclei) invalid

Reaction-limited nucleation rate model [6]

$$2Ag_i \rightarrow (Ag_i)_2$$

X Inconsistent under steady-state conditions

→ Transient dose-rate dependent analysis

$J \propto R_{(Ag_i)_2} = kc_{Ag_i}^2 = \xi \dot{d}^{2\hat{\beta}}$

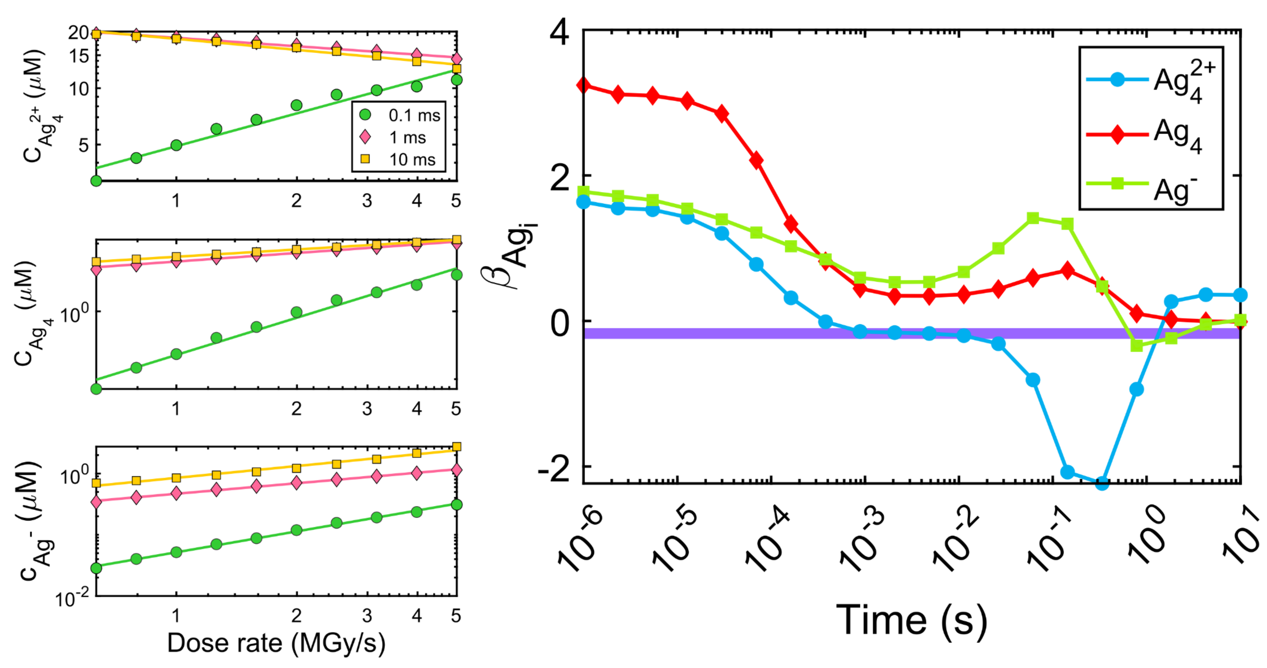
Reaction-limited growth

J: nucleation rate
$R_{(Ag_i)_2}$: generation rate
k: reaction rate constant
$\hat{\beta}$, ξ: fitting parameters

Transient radiolysis modeling

Reaction-limited cluster-cluster aggregation

consistent within 1 – 10 ms



Nucleation described by Ag_4^{2+}

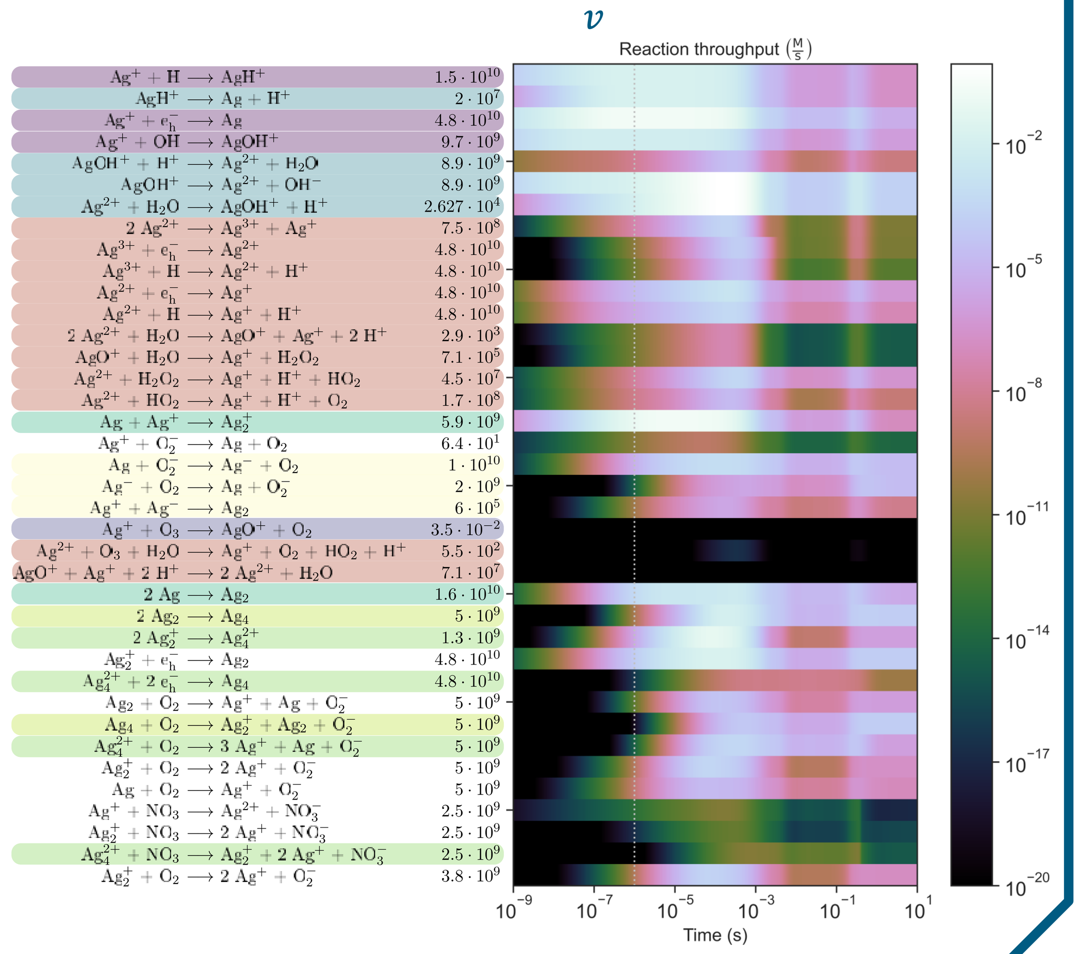
Sanity check: a concentration $c_{Ag_4^{2+}} \approx 10\ \mu M$ and diffusivity $D \approx 10^{-12}\ m^2s^{-1}$ yields a characteristic collision time of **1 ms**

Reaction throughput

How much traffic through each individual reaction?

→ reaction specific generation rate

$$\mathcal{R}_u(t) = k_u \prod_v c_v(t)$$



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