Nucleation of metallic nanoparticles in liquid phase

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Little is known about the detailed mechanisms that trigger the growth of particles in liquid phase, even for simple elemental metal nanoparticles that are routinely synthesized in such environments. The LaMer particle-growth model most simply considers nucleation to occur instantaneously. The classical nucleation theory, at least, provides guidelines about energy hurdle and critical cluster size. Yet, both of these models describe particle growth by attachment of single molecules or single atoms, whereas particle interactions are entirely ruled out. Particularly for more complex systems, like $CaCO_3$, there is plenty of evidence that these simple theoretical models fail to describe the multi-step mechanisms experimentally documented.

We have developed liquid-phase in-situ approaches in the scanning transmission electron microscope to uncover nucleation and growth mechanisms of simple metallic elements, such as Au, Pt or Pd or alloys thereof. Our approaches are based on employing either graphene-based liquid cells (see, e.g. [1,2]) or liquid nanoreactors of vacuum compatible ionic liquids (see, e.g., [3]), both allowing atomic scale observations to be done with single atom sensitivity (see Fig. 1).

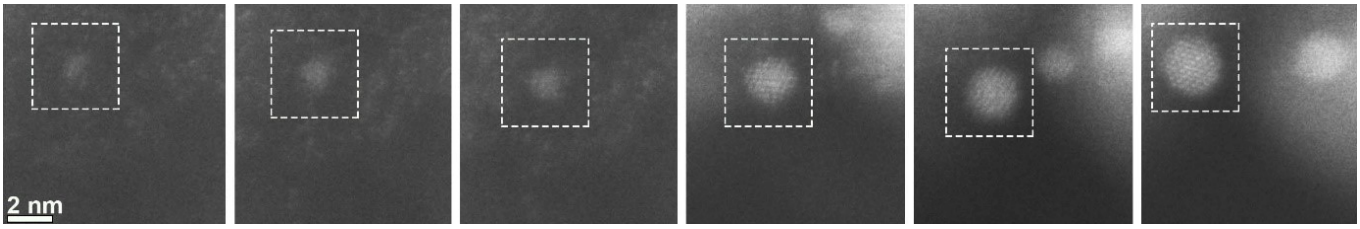

Fig. 1 Nucleation of a Pt particle in an aqueous solution in a graphene-based liquid cell. Reproduced from reference [4].

Our experiments reveal that even the simple metal systems investigated in our studies do not follow an ordinary one-step mechanism. These nucleation and particle-growth reactions consist of several steps where, for instance, particle interactions are of critical importance in the growth process [3]. In the case of gold nucleating in aqueous solution, we see that the immediate environment of a growing particle can be described as a cluster cloud that dynamically acts as source and drain of matter during the growth and crystallization steps [1]. Based on volume and surface energies of the corresponding bulk materials, we developed a systematic model that allows different steps in nucleation and particle-growth reactions to be predicted.

[1] W. Dachraoui, D. Keller, T. R. Henninen, O. Ashton, R. Erni, *Nano Letters* **2021**, *21*, 2861-2869.
[2] W. Dachraoui, M. I. Bodnarchuk, R. Erni, *ACS Nano* **2022**, *16*, 14198-14209
[3] D. Keller, T. R. Henninen, R. Erni, *Nanoscale* **2020**, *12*, 22511-22517.
[4] W. Dachraoui, T. R. Henninen, D. Keller, R. Erni, *Scientific Reports* **2021**, *11*, 23965.