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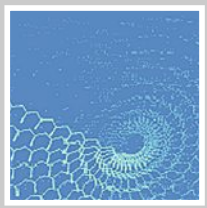

Polymer and Colloid Highlights

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Liquid Phase Studies of Nanomaterials

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Liquid cell transmission electron microscopy (LCTEM) is a relatively new technique enabling researchers to study dynamic phenomena in materials sciences, life sciences and electrochemistry. LCTEM has proved to be a remarkable tool for observing colloidal nanoparticle syntheses at fairly high temporal and spatial resolutions offered by transmission electron microscopy (TEM). Though the idea of observing syntheses in their native media is not new, a practical approach has only been made possible through massive improvements in microfabrication technology to fabricate liquid cells.[1] The idea is to use thin window materials such as SiN membranes (50 nm or less) to encapsulate tens of cubic nanometers of liquid in a stable thin profile suitable for TEM imaging considering the vacuum environment of the microscope (Fig. 1).

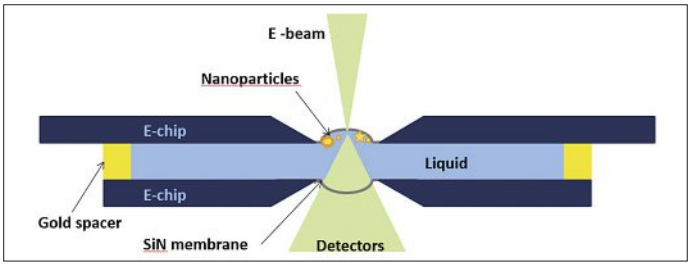

Fig. 1. Schematic cross-section view of a liquid cell in scanning TEM mode employing a focused electron beam.

New window materials such as graphene membranes are also increasingly employed albeit with certain challenges to further improve the spatial resolution of processes under study.[2] A major challenge for LCTEM experiments concerns electron beam effects which can result in the radiolysis of the solvent medium, thus making the interpretation of processes much more complex. Two distinct strategies have evolved to deal with such effects, *i.e.* either to suppress them as in biological and operando electrochemical studies or to exploit them for beam-induced growth of inorganic nanostructures. We have used electron beam irradiation in a controllable fashion to fabricate metallic nanoparticles of various morphologies. The main goal is to develop an understanding of the nucleation and growth dynamics of nanocrystals as well as to differentiate the kinetic effects (flow of matter) and thermodynamic effects (equilibrium of nanostructures). It is found that even in simple solution chemistries and employing only one type of precursor salt, *e.g.* $HAuCl_4$, the growth morphology varies as a function of the applied electron dose rate (Fig. 2), the solute concentration and the solvent nature.[3] The electron beam can thus be utilized in a tunable fashion to manipulate the concentration of different types of radical species (e_{aq}, $OH^{\bullet}$ etc.) within the solvent, in essence affecting the growth mechanism. Current sample holders additionally incorporate capabilities of flow, mixing, biasing and heating different chemical reagents during the course of experiments that allow *in situ* observations of different chemical reactions. This aspect is increasingly used to synthesize core-shell nanoparticles such as Ag@Au and Pt@Au.[4] Important information is obtained by observing the kinetics of deposition of one type of metal on top of another. Such studies are pivotal for improving our understanding of self-assembly processes increasingly employed in chemistry labs for large-scale production of complex nanoparticles.

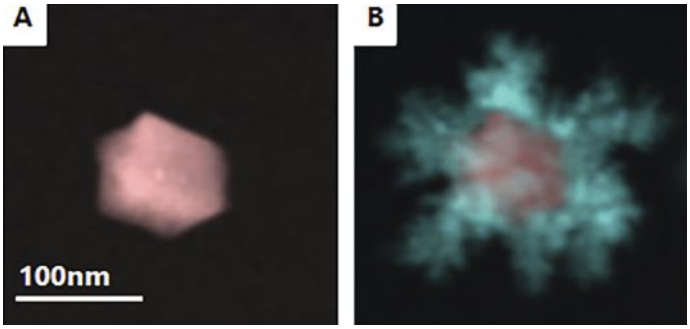

Fig. 2. Transition from reaction limited to diffusion limited growth. A) Annular dark-field scanning TEM image of a faceted Au nanostructure formed at an electron dose rate of 0.74 $e^-/Å^2s$ in 1 mM $HAuCl_4$ aqueous solution. B) At higher electron dose rate of 2.80 $e^-/Å^2s$ the growth mode changes to dendritic forming a shell over the faceted nanoparticle.[3]

More complex applications include seed-mediated synthesis of stellated nanocrystals such as Au nanostars[5] for which LCTEM can reveal the underlying atomic-scale mechanisms as well as facet restructuration processes due to surface diffusion effects. Since a plethora of research areas are currently accessible through LCTEM, there is an imminent need to quantify the unavoidable electron beam effects in liquids. This calls for developing detailed kinetic models for better understanding of the radiolysis processes and the interconnected nature of the chemical reactions involved.

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[1] F. M. Ross, *Science* **2015**, *350*, 6267.
[2] M. Textor, N. de Jonge, *Nano Lett.* **2018**, *6*, 3313.
[3] Y. Zhang, D. Keller, M. D. Rossell, R. Erni, *Chem. Mater.* **2017**, *29*, 10518.
[4] E. A. Sutter, P. W. Sutter, *Nanoscale* **2017**, *9*, 1271.
[5] N. Ahmad, G. Wang, J. Nelayah, C. Ricolleau, D. Alloyeau, *Nano Lett.* **2017**, *7*, 4194.

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