

In-Situ Liquid Cell Electron Microscopy of the Solution Growth of Core-Shell Nanostructures

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Real-time electron microscopy observations of processes in wet environments, i.e., solutions, liquids, etc. have become possible only very recently with the development of electron beam transparent cells, in which a liquid layer is trapped between two ultrathin, electron-transparent membranes. Liquid-cell transmission electron microscopy (TEM) and scanning TEM (STEM) have attracted a lot of interest as they give direct insight into processes such as solution synthesis of nanostructures [1, 2], electrochemistry [3], biological phenomena, etc.

Here we present our in-situ liquid cell STEM observations of solution growth of metal nanoparticles and composite heterostructures of Pd and Au. Bimetallic nanoparticles and composite heterostructures, such as core-shell nanoparticles, are of interest due to the promise of enhanced and tunable functional properties, for example increased catalytic activity and selectivity in a number of chemical reactions. Au-Pd bimetallic nanoparticles and core-shell nanostructures, in particular, demonstrate higher catalytic activity compared to monometallic catalysts in a variety of reactions [4].

We follow in real time and with high spatial resolution the homogeneous nucleation and growth of Pd, Au, and Au-Pd nanoparticles in dilute aqueous Pd and Au salt solutions, respectively. The growth exploits the fact that high-energy electron beams affect aqueous solutions containing metal ions or charged complexes through the generation of hydrated electrons and other radicals. Hydrated electrons (e_{aq}^-), for instance, are strong reducing agents that react with complex ions of most metals at a diffusion-controlled rate. Their transfer from solution reduces the metal ions to zero-valent metal atoms or atom clusters. By incorporating nanoscale seeds of different materials, i.e. Au (figure 1) and TiO_2 in the solution we investigate the templated growth of Pd, Au or Au-Pd on these seeds, and can thus follow the formation of complex nano-heterostructures. Real-time STEM observations allow us i) to follow the evolution of the growing material and the formation of heterostructures; ii) to directly identify different growth processes, i.e. growth in the solution, on the seed particle surface, or combinations of the two; and iii) to determine variations in growth rates at different surface sites on nanoparticles. The analysis of the Pd and Au incorporation at different distances from a focused electron beam provides a quantitative picture of the growth process, and shows that the growth is limited by the diffusion of e_{aq}^- in the solution [5] and by the mobility of the zero-valent metal monomers. We demonstrate that a judicious choice of the material and the morphology of the seeds provides control over the formation of a variety of heterostructures, such as core-shell nanoparticles with different shell morphologies, hollow-shells, etc. all of which promise enhanced and tunable functional properties, for example increased catalytic activity and selectivity in a number of chemical reactions.

References:

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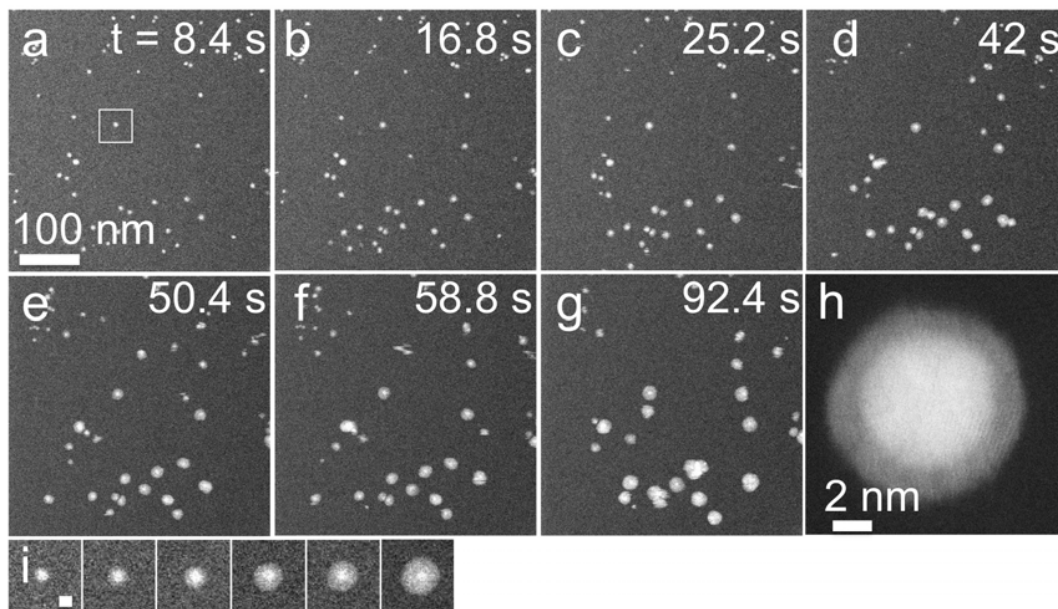


Figure 1: Pd growth on 5 nm Au nanoparticles seeds. **a** – Initial dark-field STEM image of an ensemble of 5 nm Au nanoparticles in 10 μM aqueous PdCl_2 solution. Electron dose per image: $150\text{e}^-/\text{\AA}^2$. **a** – **g** Time lapse series following the growth of Pd on the Au seeds over 92.4 s. **h** – High-resolution Z-contrast image of a Au-Pd core-shell nanoparticle formed by Pd growth on the Au seeds. **i** – Image series showing the growth on an individual particle marked by a white frame in **a** (scale bar: 5 nm).