

Direct Observation of the Growth of Au-Pd Core-Shell Nanoparticles Using Low-Dose STEM with the Liquid Cell *in situ*

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Bimetallic (BM) nanoparticles (NPs) are widely used as the catalysts in several industrial reactions. The catalytic activity in these systems is largely determined by the morphology and crystalline structures of the NPs, which can be controlled through the nucleation and growth process. However, despite numerous reports, the early stages of nucleation and growth mechanisms remain unexplored.[1, 2] The development of *in situ* liquid cell electron microscopy allows seeing such phenomena in real time at near-native reaction environment and more insight phenomena can be obtained.[3, 4] We present here the direct observation of the formation of Au-Pd core-shell (CS) NPs obtained with continuous flow fluid cell platform using high angle annular dark field scanning transmission electron microscopy (HAADF-STEM), while maintaining low dose imaging conditions. Our experimental setup helps in gaining a better understanding of continuous flow fluid cell experiments suitable for generating near-native reaction environment for the *in situ* experiments.

The fluid cell was assembled by sandwiching Au NPs solution between the two SiN windows with 100 nm spacer. The near-native reaction environment was generated inside the fluid cell by sequentially flowing Pd precursor and ascorbic acid as a reducing agent), while using low dose STEM conditions. **Figure 1** shows the STEM images of NPs in the fluid cell chamber. Au NPs were imaged (**Figure 1a**), after which Pd precursor solution was pumped into the reaction chamber, allowed to incubate with the Au NPs, and imaged again (**Figure 1b**), revealing no observable changes in the nanostructures. After flowing ascorbic acid (AA), the formation of CS structures were observed, as shown in **Figure 1c**. Evolution of NP structures and that of the associated Z-contrast of HAADF-STEM images was tracked in ROIs marked in **Figure 1a - c**. The nanoparticle denoted by a white rectangle grew into an isotropic core-shell structure, with more detailed record of its formation shown in **Figure 2a**. The initial rapid growth of Pd shell along the $\langle 111 \rangle$ direction, consistent with the preferential chemisorption of CTAB on the $\{100\}$ crystal facets of Au NPs and subsequent rapid deposition of positively-charged Pd ions, is followed by the rearrangement of the newly formed Pd shell to produce denser, more ordered structure, as manifested by the decrease of thickness along $\langle 111 \rangle$ noted at 285 sec, as well as by a slight enhancement of the overall Z-contrast. Following this ordering, the Pd (100) surface is stabilized to form the nanocube and yields a core-shell Au-Pd structure. This direct visualization of growth is in good agreement with previously reported *ex situ* studies.

The growth of Pd shell thickness over Au core for different times is presented in **Figure 2b**. The electron dose rate is calculated at $0.1 \text{ e}^-/(\text{\AA}^2\text{s})$ during imaging; however the interaction of electrons during the movie recording resulted in absorbing of additional electrons by the sample, leading to a higher cumulative electron dose, as noted in **Figure 2a** for each frame. The CS Au-Pd NPs were obtained only in the presence of reducing agent (AA), while no core-shell formation attributed to the electron beam effects was detected. Despite the low-dose STEM

imaging, the radiolysis of Pd precursor and AA needs to be taken into consideration. These studies are currently extended to investigate the growth mechanism of a variety of NPs with controllable morphologies and compositions, and the obtained knowledge will aid in designing advanced nanoparticles with enhanced properties.

References:

- [1] Y. Xiang *et al*, Nano Letters, **2006**, 6, 2290-2294.
 [2] Y. Xia, *et al*, Angewandte Chemie International Edition, **2009**, 48, 60-103.
 [3] F. M. Ross, Science, **2015**, 350, 6267.
 [4] M. Williamson *et al*, Nature Materials, **2003**, 2, 532-536.
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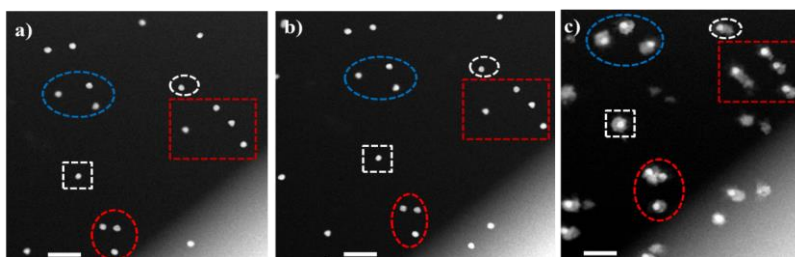


Figure 1. STEM imaging in liquid cell, a) Only Au NPs, b) after flowing Pd precursor, c) AuPd CS NPs formed after flowing ascorbic acid (AA) into the liquid cell with Au NPs and Pd precursors. Scale bar: 200 nm. The Au NPs represented by dotted square (white) in (a) and (b) changes into the core shell structure in (c). The detailed investigation of this structure is presented in **Figure 2**. Similarly, Au NPs represented by dotted oval (white, blue and red), in (a) and (b) grows into the asymmetrical core shell structure in (c) with non-uniform growth of Pd shell.

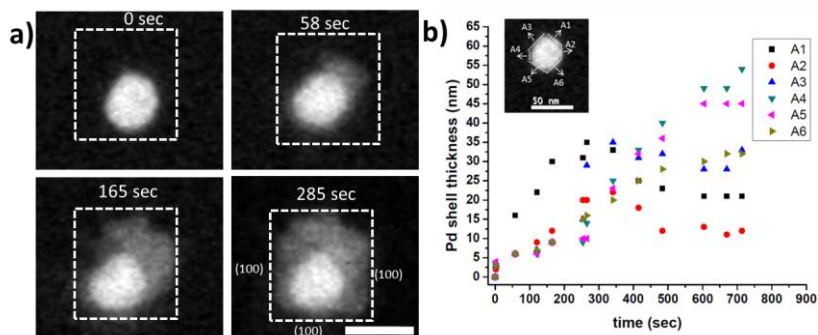


Figure 2. a) Snapshots HAADF-STEM images of the growth of Pd shell on the individual Au nanoparticle after flowing ascorbic acid; inset shows the time and electron dose on that frame. b) Thickness of the formed Pd shell as a function of time after flowing AA, measured along six directions (A1 – A6, inset), Scale bars: 50 nm.