

Probing the Dynamics of Phase Transformation in Nanostructures by STEM Imaging and Spectroscopy

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The phase transformation is commonly used to design functional materials with desirable structure and properties. The physics and chemistry at the atomic scale guide the transformation of these materials. *In situ* scanning/transmission electron microscopy (S/TEM) is suitable to gain insight into the transformation process at atomic resolution by applying a variety of stimulus (heating, biasing, cooling, strain, etc.) in combination with advanced techniques such as STEM diffraction imaging (4D STEM) and electron energy-loss spectroscopy (EELS). In addition, the electron beam within the microscope can be well controlled to emulate a reducing environment, inducing phase transformations as well. In this talk, we present our TEM studies of electron beam sensitive materials to demonstrate the capability of advanced S/TEM for probing the dynamics of phase transformation and chemical bond change: (1) dynamics of electron beam induced formation of nanoparticles from a precursor captured at low electron dose with aberration-corrected TEM; (2) thermally induced bond cleavage and formation within a metal-organic framework captured by vibrational electron energy-loss spectroscopy (EELS) in combination with *in situ* TEM imaging.

We employed *in situ* aberration-corrected TEM with a well-controlled electron beam to observe the transformation of K_2PtCl_4 precursor to Pt nanoclusters. The pristine structure of the K_2PtCl_4 was revealed at sub-Å resolution with all K, Pt, and Cl atoms resolved. The *in situ* experiment revealed a rapid transformation from the precursor to the nanocluster even under low electron dose (Figure 1A, B). Radial integration of the fast Fourier transformation (FFT) of the sequential TEM image series reflect the radial distribution function and correspond to atomic pairs with certain bond lengths, allowing for identification of the sequence of bond cleavage and cluster formation (Figure 1C). The analysis of the FFT reveal a stepwise mechanism wherein the K_2PtCl_4 precursor first decomposes into K^+ and $PtCl_4^{2-}$ owing to the weaker ionic bonding. The $PtCl_4^{2-}$ then decomposes into $PtCl_2$ and Cl^- . This second stage has not been reported, but is revealed here from the FFT of the high resolution images acquired under a low dose electron beam. Removal of some K species causes the lattice to become unstable and compounds such as $PtCl_2$, KCl , and Cl_2 move about. Finally, $PtCl_2$ is reduced to zero-valent Pt and the formation of the Pt nanocluster either nucleate or migrate along the surface to add to other nuclei. Our findings demonstrate a staged reduction and nucleation of Pt following the order of chemical and bonding energy.[1]

Sequential bond cleavage and formation was also observed during *in situ* heating of a zirconium-based metal-organic framework. Individual FFTs of an image series at increasing temperatures were integrated radially, revealing the inter-zirconium distance decreased at increasing temperatures. Vibrational EELS was performed at 60 kV using a monochromated, spherical aberration-corrected Nion UltraSTEM with an energy resolution of 5.7 meV to investigate the mechanisms of the lattice contraction. We observed the formation of disulfide bonds at 250 °C. At higher temperatures, the weak disulfide bond was cleaved and decarboxylation occurred, leading to a second stage of contraction in the lattice. The *in situ* vibrational EELS results were corroborated with *ex situ* X-ray photoelectron spectroscopy. This sequential transformation was shown to occur in step and at varying temperatures through a combination of TEM imaging and vibrational EELS.

In situ studies of materials transformation using advanced TEM techniques can reveal details of a transformation process previously not observed. By combining the atomic resolution imaging afforded by aberration-corrected TEM with other tools, a direct understanding of structure changes can be correlated with chemical changes, giving insight into the mechanism which other material systems can be transformed.

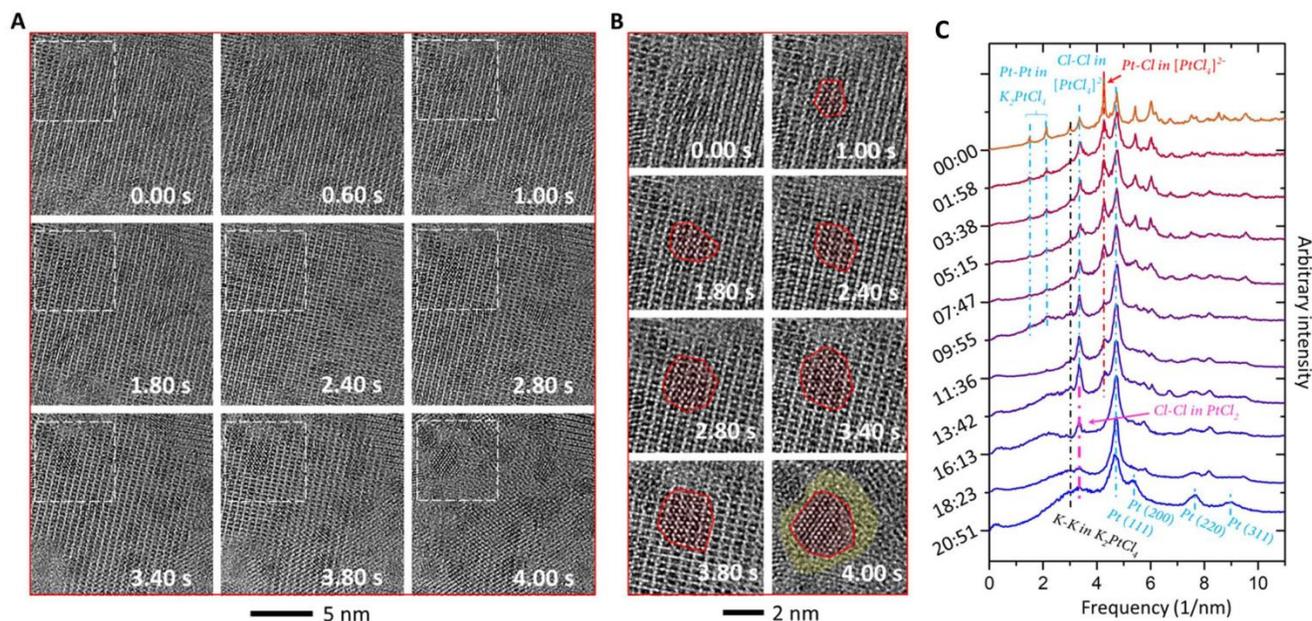


Figure 1. (A) Sequential TEM images showing the evolution of K_2PtCl_4 into Pt nanoclusters. The Pt nucleation process is showing in the zoomed-in images in (B) from the white dashed box in (A). The red contour lines show the edge of the newly formed Pt cluster. The yellow region highlights areas void of lattice after Pt cluster formation. (C) Radially integrated FFTs from an extended image series showing the sequential bond cleavage and formation during the transformation process.

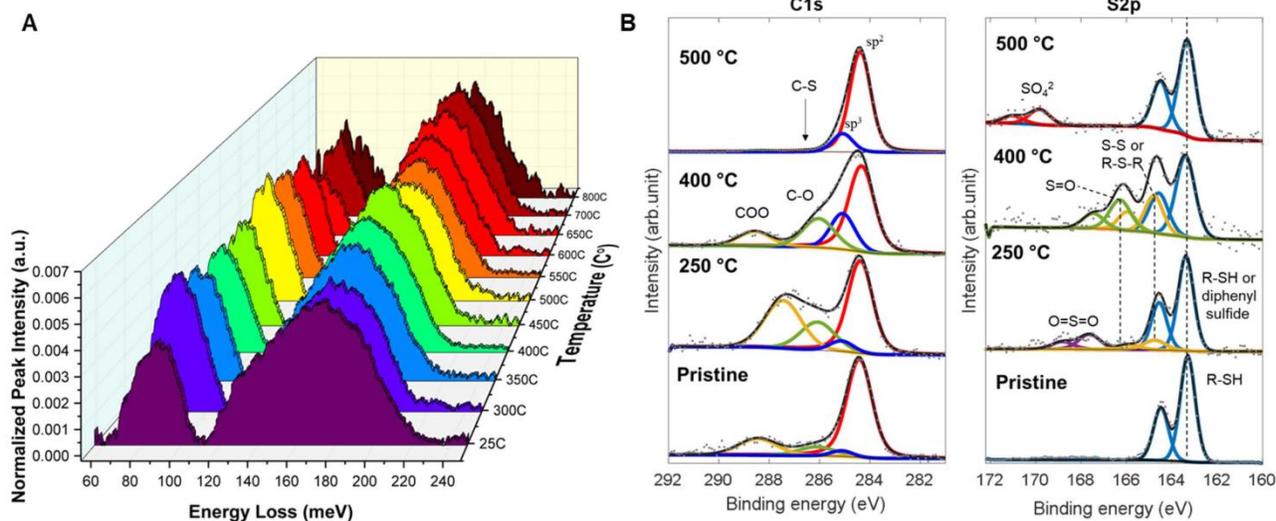


Figure 2. (A) Vibrational EELS signal acquired at increasing temperatures. The peak from 60–110 meV is attributed to the C-S and S-S bonds. The peak from 115–225 meV is attributed to the aromatic C-C and carboxyl bonds. (B) Ex situ X-ray photoelectron spectroscopy of C1s and S2p peaks at various temperatures corroborating the formation and cleavage of the disulfide bond and the decarboxylation process.

References

[1] W. Gao, *et al. Sci. Adv.* **2019**, 5, eaau9590

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