

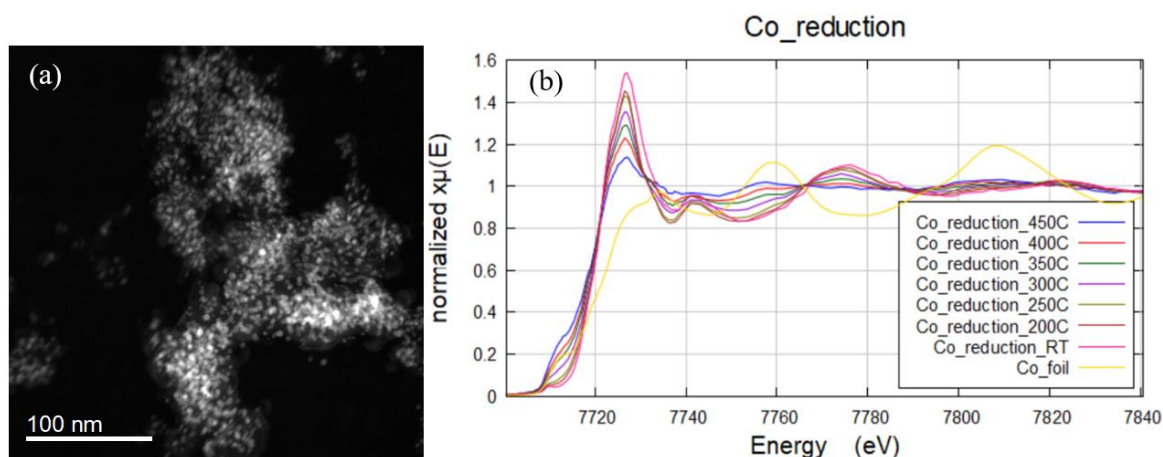
## Using in situ electron energy-loss spectroscopy (EELS) and X-ray fluorescence microscopy (XFM) to characterize Co-Pt nanoparticles

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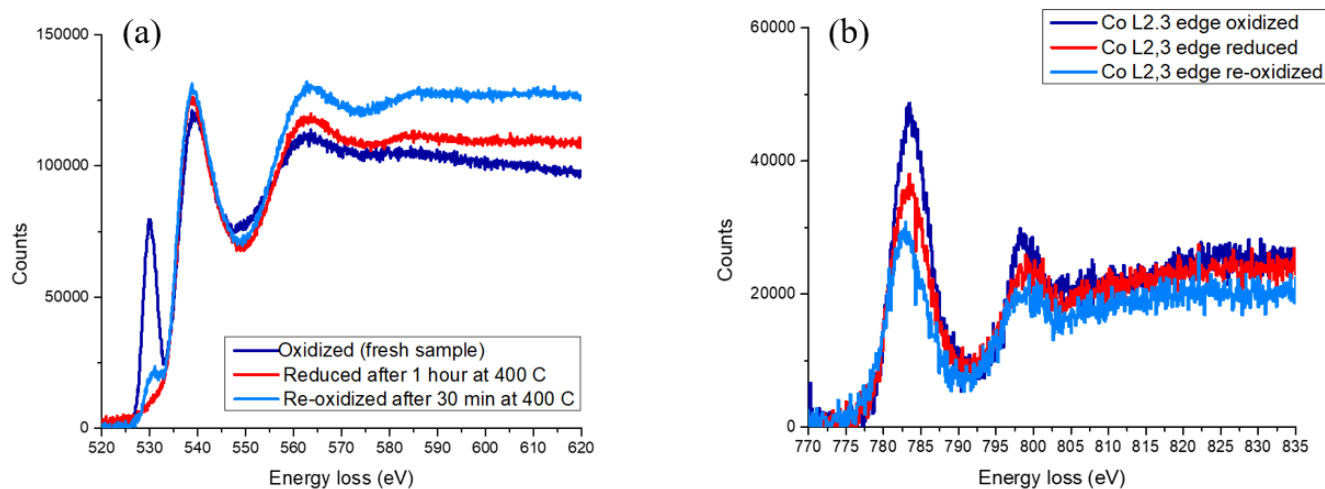
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Co-Pt nanoparticles have enormous potential and are widely used catalysts for the oxygen reduction reaction (ORR) in fuel cells. Bimetallic particles were designed to reduce the use of expensive Pt, by diluting the Pt atoms into Co and keeping them well dispersed on the surface. Hence, this process significantly optimized the use of Pt for catalytic reaction. However, little is known about the migration of Pt atoms within the Co-Pt ensemble, especially during the reaction. Pt atoms are less optimized if they migrate towards the core of particles or segregate by forming clusters, ultimately reducing the catalytic properties.

In this work, 10-nm Co-Pt nanoparticles supported on carbon and exposed to O<sub>2</sub> and H<sub>2</sub> were investigated with a multimodal approach. In situ scanning transmission electron microscopy combined with electron energy-loss spectroscopy (STEM-EELS) and in situ XFM was performed to track dynamical restructuring effects. I will first review how we took advantage of a direct detection system for obtaining in situ EELS spectra. The improved signal-to-noise ratio makes it possible to perform fine structure analysis on the data and track chemical changes in metallic elements. This is the same approach used with X-ray absorption spectroscopy (XAS) to determine the valence state or the coordination number of elements [2]. I will then focus on in situ XFM where the sample underwent the same redox cycle. In situ XFM data were obtained with a 10 μm beam, hence providing information of a larger number of particles as the beam used for STEM-EELS is smaller than 1 Å. This unique approach can track the structure of the catalysts under realistic conditions and reveal the valence state during oxidation and reduction: Changes of the morphology as well as modification of the oxidation and coordination numbers were observed and could be interpreted as a degradation mechanism of the Co-Pt system. Both in-situ data sets are complementary and provide chemical information at different length scales that will guide the future design of more active nano-catalysts [3].



**Figure 1.** (a) Ex situ dark-field STEM image of the particles on carbon. (b) In situ XFM experiment with Co K edges collected. The sample was exposed to H<sub>2</sub> and the temperature was progressively increased.



**Figure 2.** In-situ EELS spectra collected for the Co-Pt particles. (a) O K edge. (b) Co L2,3 edges.

## References

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- [4] This work was supported as part of the IMASC, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0012573. This research used the XFM Beamline at the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704. This work was carried out in part at the Singh Center for Nanotechnology at the University of Pennsylvania which is supported by the National Science Foundation (NSF) National Nanotechnology Coordinated Infrastructure Program grant NNCI-1542153. Additional support to the Nanoscale Characterization Facility at the Singh Center by the University of Pennsylvania Materials Research Science and Engineering Center (MRSEC) supported by the National Science Foundation (DMR-1720530) is acknowledged.