Carbon Oxidation Kinetics by Single Nanoparticle Mass Spectrometry

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This talk will describe use of single nanoparticle mass spectrometry (NPMS) to measure sublimation and oxidation kinetics of individual laser-heated carbon nanoparticles (NPs) trapped in the gas phase. The goal is to measure the effects of NP heterogeneity on kinetics, specifically the effects of NP-to-NP variations in size, shape, and nanostructure, and the effects of the distribution of surface sites on *individual NPs*, which evolve with time. In addition, we measure emission spectra for individual NPs over the 400 to 1650 nm range.

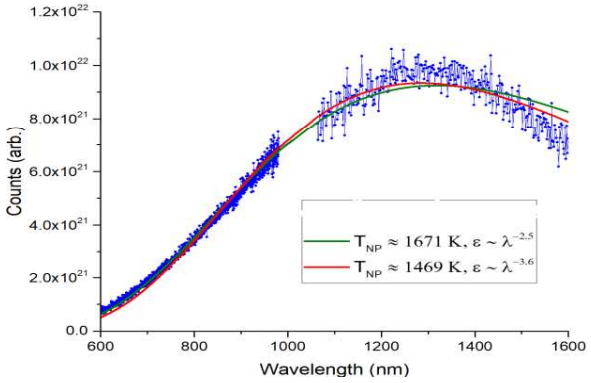

Fig. 1. Single NP emission spectrum

In NPMS, a single NP is trapped in an AC quadrupole trap, laser heated to incandescence, and its motion is detected optically. From the motional frequency, it is possible derive the mass M and charge Q of the NP, and since the measurement is non-destructive, kinetics for sublimation, addition reactions, and oxidation can be followed over ~5 orders of magnitude by tracking M vs. time. The temperature range is roughly 1400 K to 2500 K. In addition, the number of reactive sites on each individual NP can be measured using a site titration process, providing NP-by-NP correlations between the number of reactive sites and the kinetics. NP temperature (TNP) is determined simultaneously with kinetics, by measuring the emission spectrum using a pair of array spectrographs. Fig. 1 shows an example single NP emission spectrum acquired in 10 sec, along with fits assuming two simple models for the variation of emissivity with λ. Note that the spectrum shows significantly greater curvature in the IR that either model predicts. Fig. 2 shows an example of kinetics measured with simultaneous T_{NP} determination, in this case for sublimation of a graphite NP with initial mass of 28.007 MDa, heated with a CO_2 laser. During the initial period, T_{NP} drifted from ~1594 to ~1586 K, and the sublimation rate averaged 11 carbon atoms/sec, or ~4 ppm/sec. When T_{NP} was raised to ~1649 K, the rate increase to 50 atoms/sec, and raising the temperature to ~1666 K increased the rate to 63.5 atoms/sec, followed by a drop to 8 atoms/sec when T_{NP} was returned to 1575 K. When automation of the experiment is complete, the laser stability, frequency of T_{NP} determination, and range of rates that can be studied will increase substantially.

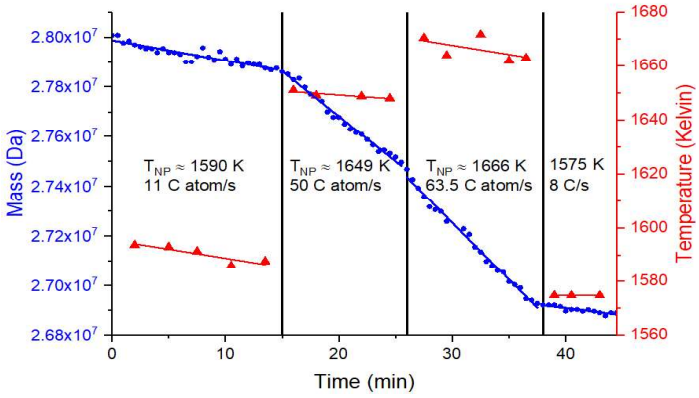

Fig. 2. Sublimation kinetics for a 28 MDa graphite NP