

# Coalescence and Sintering of Platinum Nanoparticles: In-situ Observation by Aberration-Corrected HAADF STEM

M.A. Asoro<sup>1</sup>, D. Kovar<sup>1</sup>, Y. Shao-Horn<sup>2</sup>, L.F. Allard<sup>3</sup> and P.J. Ferreira<sup>1</sup>

<sup>1</sup>Materials Science and Engineering Program, University of Texas at Austin, Austin, TX 78712, USA

<sup>2</sup>Dept. of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

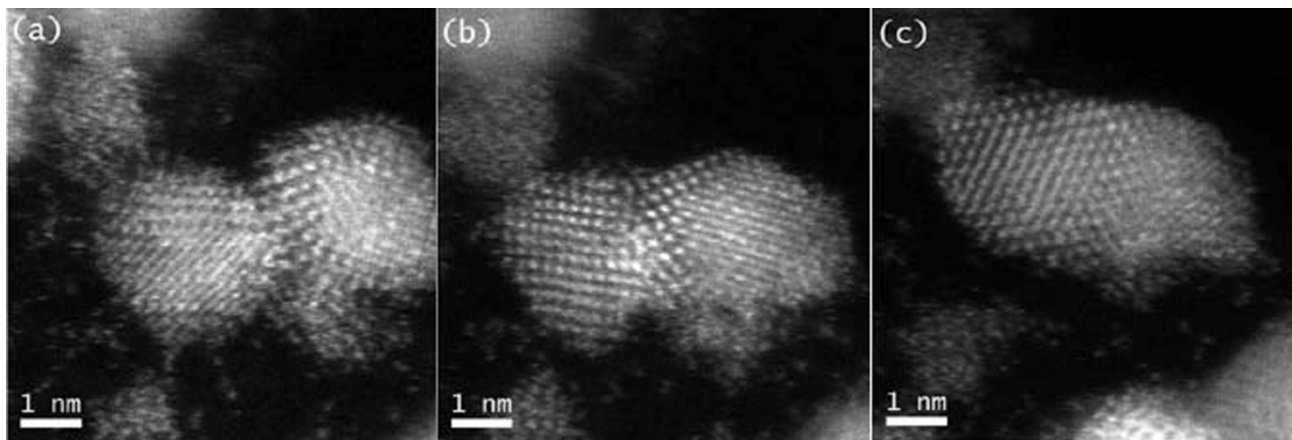
<sup>3</sup>Materials Science and Technology Division, Oak Ridge National Laboratory Oak Ridge, TN 37831 USA

Nanoparticles are currently of great scientific interest due to their large number of possible applications - such as catalysts in fuel cells, patterned lines in microelectronics and as delivery vehicles for medicine. However, during processing or usage, nanoparticles have a strong tendency to agglomerate and coalesce over short time scales, even at room temperature, which can lead to significant changes in behavior and performance. Although a reduction in sintering temperature is predicted from simple scaling models such as Herring's law, it is important to know the relevant diffusivities to predict sintering kinetics of nanoparticles.

In this work, we have used an aberration-corrected JEOL 2200FS scanning transmission electron microscope (STEM), equipped with a high-angle annular dark-field (HAADF) detector to monitor the sintering process of Pt nanoparticles with 2.8 nm nominal size. This experiment provides real-time dynamic information for a direct investigation of the evolution of sintering, which post-mortem TEM observations are not capable of conveying.

A sequence of aberration-corrected HAADF STEM images showing the coalescence of Pt nanoparticles under the influence of the electron beam at ambient temperature is shown in Fig. 1. To minimize the influence of the electron beam on the sintering process, the beam was turned off after each image was taken. The particle radius, neck radius and dihedral angle were measured from the HAADF STEM images, using the Gatan DigitalMicrograph software. These values can subsequently be used to calculate fundamental variables, such as surface diffusion coefficients and grain boundary mobility. For example, if we consider surface diffusion to be dominant, the surface diffusion coefficient,  $D_s$  is calculated to be within the range  $3.47 \times 10^{-20} \text{ cm}^2/\text{s} - 1.19 \times 10^{-19} \text{ cm}^2/\text{s}$  for Pt nanoparticles, which agrees well with the calculated value of  $D_s$  for bulk Pt ( $1.13 \times 10^{-19} \text{ cm}^2/\text{s}$ ).

However, as the calculations are based on a single experiment (Fig. 1), we should take these results with caution. Nevertheless, in-situ aberration-corrected HA-ADF STEM proves to be a valuable technique to study the coalescence of very small nanoparticles, particularly those which are supported on a carbon substrate, such as the case of Pt catalysts for fuel-cell applications.



**Fig. 1:** A sequence of STEM HA-ADF images showing the coalescence of Pt nanoparticles. The images from left to right were recorded at intervals of 20 seconds.