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doi:10.1017/S1431927613009185

Microsc. Microanal. 19 (Suppl 2), 2013

High-Resolution STEM Analysis of Nanoparticle Materials

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Z-contrast scanning transmission electron microscopy (STEM), where the image intensity depends upon the atomic number Z, offers an extremely powerful tool to examine heavy nanoparticles on lighter support materials. Almost since the first development of STEM by Crewe and coworkers, it has been possible to locate single heavy metal atoms on low-Z backgrounds. However, with new aberration-corrected machines being developed, higher resolution can be achieved and the opportunities for analyzing small nanoparticles, and even single light atoms, are improving.

Nanoparticles offer a wide variety of important physical characteristics, ranging from useful optical or magnetic properties to high catalytic activity. Striking examples of the role that the nanoscale plays in these properties include the ubiquitous catalytic oxidation of CO by supported Au nanoparticles [1] and the wide variety of catalytic properties displayed by Au nanoparticles on different types of amorphous carbon [2]. Thus understanding the size distribution of such nanoparticles and how they change over time can be critical. In order to better study these effects we previously developed a sputtering method capable of producing a variety of nanoparticles on powdered supports [3]. The advantage of this method is that it allows nanoparticles to be produced without relying upon traditional chemical methods, thus enabling the effect of different surface treatments to be examined. By combining this technique with Z-contrast STEM we found that the lifespan and thus catalytic activity of Au on TiO_2 is heavily dependent on the surface chemistry of the support material [4]. One potential drawback of electron microscopy is that the electron beam can induce damage or other changes in the material. Figure 1 shows example images recorded of nanoparticles supported on SiO_2 as a potential catalyst material. The images were recorded at 200 kV with about 1250 electrons per pixel. Substantial changes in the shape of the nanoparticles are visible. Single Pt atoms, visible as bright spots in the image, move around between frames, causing the shapes of the nanoparticles to change. A variety of techniques can be used to minimize these effects including low-energy STEM or low-dose sequential imaging, where a series of images are obtained and aligned by post-processing [5].

While such electron beam induced changes are usually regarded as a negative effect, careful tuning of the beam energy and electron dose can be used to extract a wealth of information on atomic scale energy landscapes and dynamics [6]. A further application of sequential imaging is shown in Figure 2, which demonstrates the formation and growth of metal nanoparticles on a many-layer graphene support, acquired at 60 kV. Rafts of heavy atoms (Ru, Fe, Cu) are visible in the initial image. During the acquisition of the series, for which the area was continuously illuminated by the electron beam, the metal atoms agglomerate and begin to form particles, allowing nanoparticle growth to be directly imaged. [7]

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[7] This research was sponsored by the Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, U.S. Department of Energy (ARL, GMV, CL, SJP), and the UT/ORNL Joint Institute for Advanced Materials and the U.S. Department of Energy, Office of Basic Energy Sciences under Award Number DE-SC0004792 (JCP).

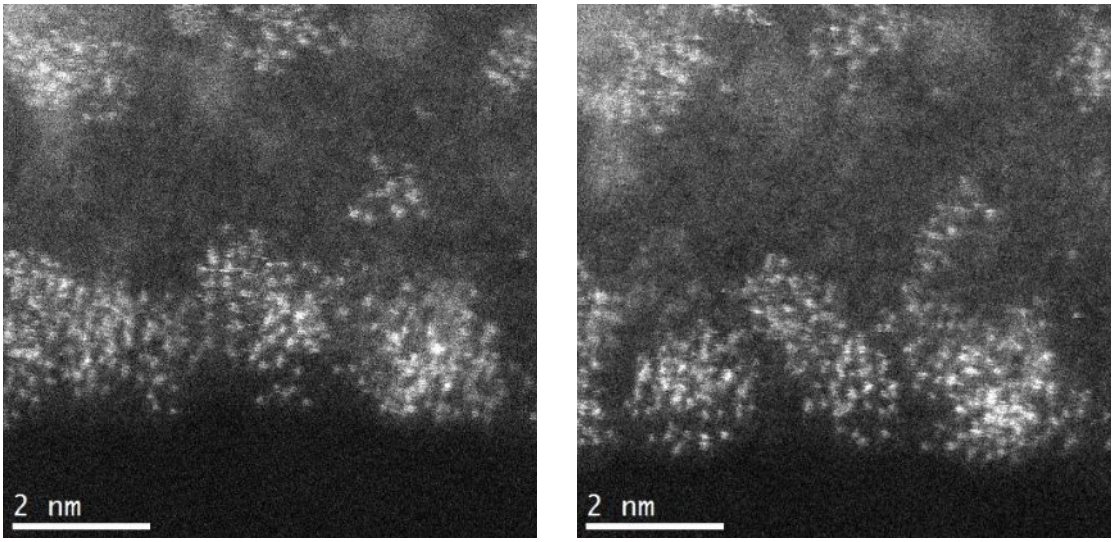

Figure 1. Frames extracted from sequential images of a prototype catalyst material acquired at about 2 sec/frame. The bright spots are Pt atoms and the support is SiO_2.

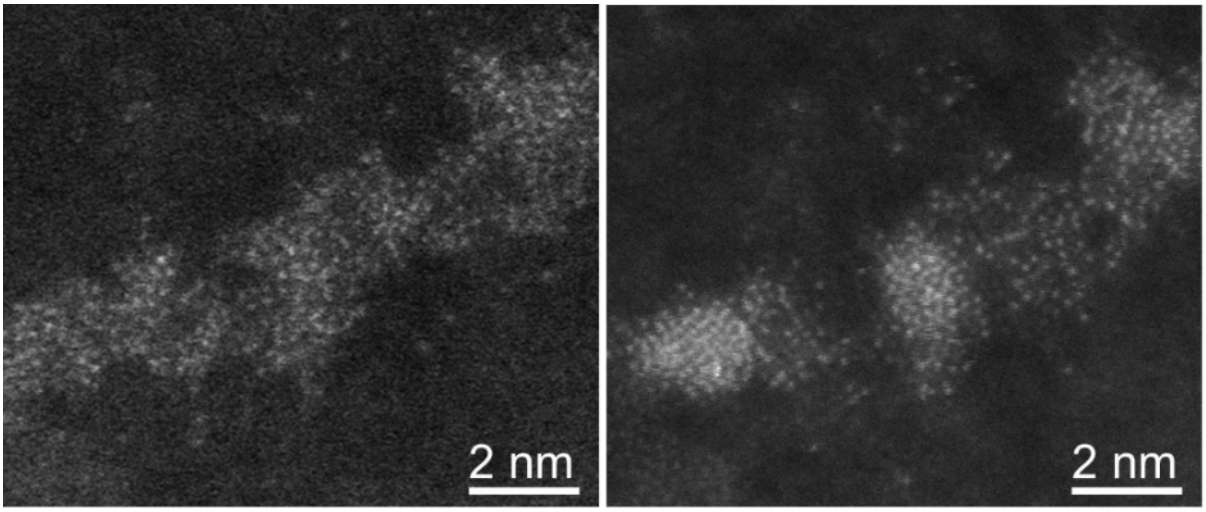

Figure 2. Aligned images showing the growth of nanoparticles from rafts of heavy atoms, (left) initial frame and (right) the same area imaged after the 200 frames sequence.