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The 3-D Pore Structure of Pd Nanoparticles as a Function of Temperature

Matthew P. Klein[1], Markus D. Ong[2], Stephen J. Fares[2], Benjamin W. Jacobs[2], David B. Robinson[2], and Ilke Arslan[3]

[1]Department of Mechanical and Aeronautical Engineering , University of California-Davis, Davis, CA 95616, USA.

[2]Sandia National Laboratories, 7011 East Ave. Livermore, CA 94550, USA.

[3]Department of Chemical Engineering and Materials Science, University of California-Davis, Davis, CA 95616, USA.

Introduction

With the increasing interest and usage of alternative energy sources, the need for reliable and efficient energy storage methods is likewise increasing. Porous nanoparticles, and in particular Pd, are being investigated for their potential use in catalysis, hydrogen storage, and electrochemistry [1]. For all of these applications, a very high surface area is desirable, with every point in the material ideally being within a few atoms of an interface. This would facilitate attributes such as high double-layer capacitance, higher reaction rates in kinetically limited interfacial reactions, and rapid charging with hydrogen [2, 3].

In order to ensure the reliable performance of these materials for such applications, the pore connectivity, diffusion, migration, and collapse must be understood for a variety of thermal treatments. To measure pore and particle sizes and distributions, techniques such as porosimetry, small angle x-ray scattering, and light scattering can be used. These techniques make characteristic quantitative measurements by averaging over large amounts of sample material. Although these techniques are good for characterizing the properties at the bulk scale, they are not capable of directly observing structural transformations of individual pores and particles while heating takes place. Conventional transmission electron microscopy (TEM), however, is capable of producing the higher resolution analysis that is needed to complement the other techniques. Unfortunately, this still only provides two dimensional (2-D) information of an intrinsically three dimensional (3-D) nanoscale material, and therefore limits the structure-property understanding of these complex materials.

Techniques

Here we use electron tomography in the scanning transmission electron microscope (STEM) [4] to elucidate the 3-D pore structure with a resolution of ~1 nm in all three spatial dimensions. For the study of inorganic materials, Z-contrast imaging in the STEM (figure 1) is the most appropriate imaging mode for the acquisition of the tilt series, as it can circumvent the problems of unwanted Fresnel and diffraction contrast due to the nature of the incoherent scattering process (which is not true for conventional TEM imaging). Data sets of images were acquired over a range of angles, every 1 .

Once the 2-D projections are acquired (figure 2(a)), the reconstruction is achieved, in simple terms, by smearing out the projection back into an object space at the angle of the original projection. Using a sufficient number of projections from different angles, the superposition of all the backprojected 'rays' will return the original object (figure 2(b)).

We apply this technique to three sets of porous Pd nanoparticles all heated to different temperatures. The first is a set of particles that have not been heated at all. The second was heated to 200 ˚C and then cooled immediately and the third was heated up to 600 ˚C and cooled immediately.

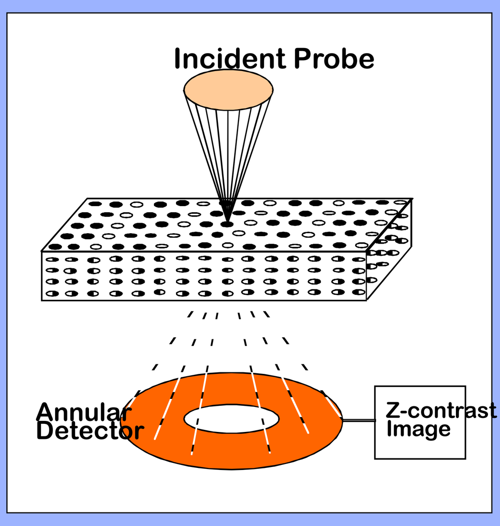

Figure 1: Schematic of Z-contrast imaging in the STEM. A focused probe is scanned across the specimen, and the scattered electrons are collected on the High Angle Annular Dark Field (HAADF) detector.

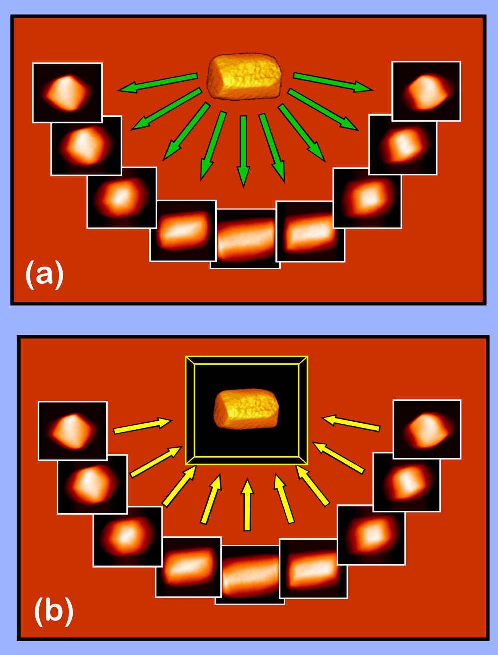

Figure 2: Schematic of a reconstruction by backprojection. (a) An object is sampled by projection of images from different angles in the microscope, then (b) reconstructed by backprojecting into the object space.

3-D Imaging of Porous Palladium Nanoparticles

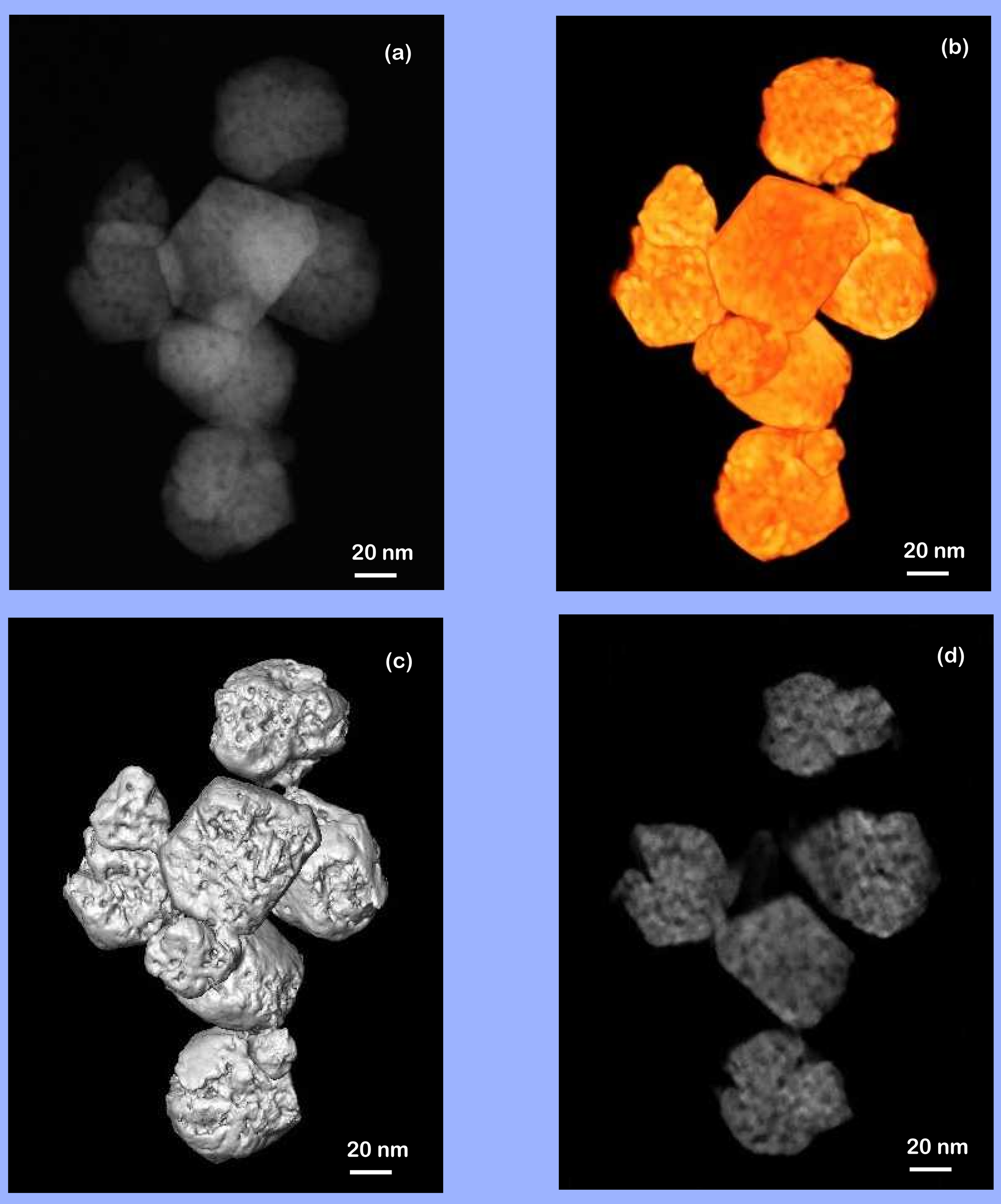

Figure 3: Unheated Pd nanoparticles (a) shows a typical STEM HAADF image. (b) is a volume-rendered tomographic reconstruction (c) is a surface render and (d) is a 1 nm slice through the reconstruction which shows the unheated pore structure.

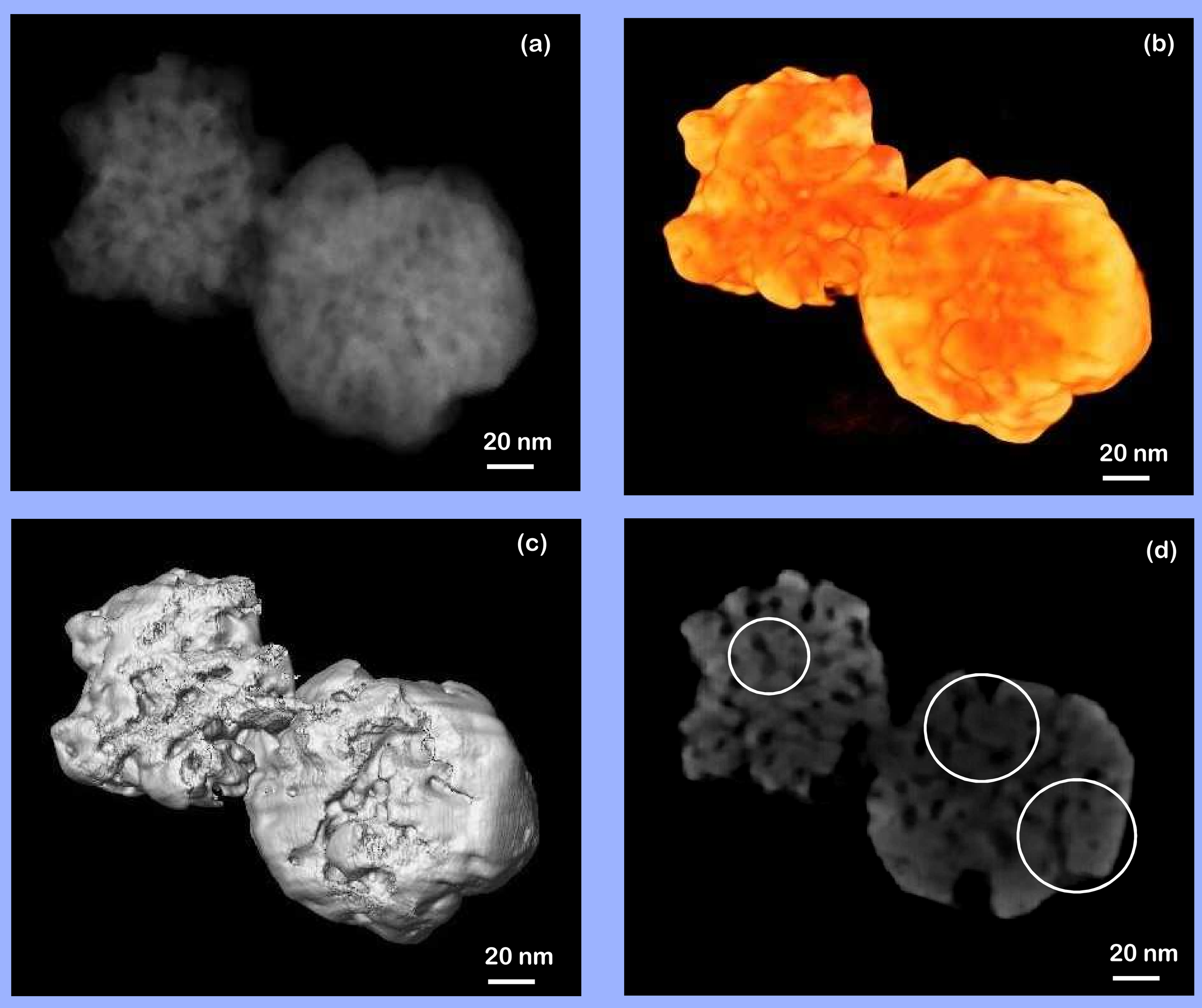

Figure 4: Pd nanoparticles heated to 200˚C (a) shows a STEM HAADF image. (b) is a volume-rendered tomographic reconstruction (c) is a surface render and (d) is a 1 nm slice through the reconstruction which shows how the pore structure is beginning to collapse. The pore structures circled in (d) show the connection and forming of small bubbles.

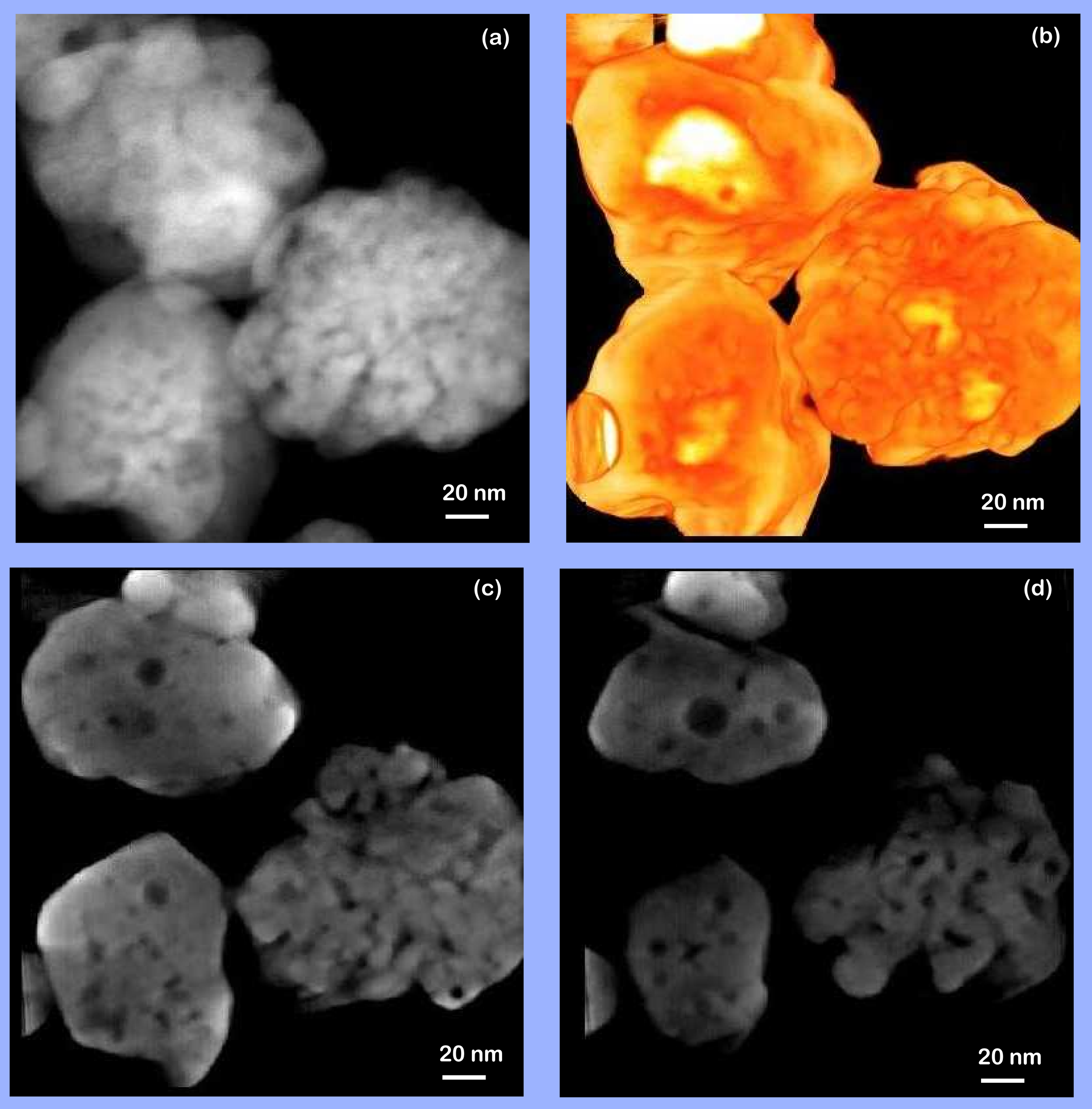

Figure 5: Pd nanoparticles heated to 600 ˚C (a) shows a STEM HAADF image. (b) is a volume-rendered tomographic reconstruction (c) and (d) are 1 nm slices through the reconstruction which show how the pore structure has fully collapsed into bubbles. The larger bubbles of ~5-10 nm are trapped inside the Pd, but upon heating to a high enough temperature, they escape to the surfaces.

References:

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Conclusions

•STEM tomography is used to reveal the size, shape, distribution, and porosity of the palladium nanoparticles. The tomograms will be further analyzed to quantify their surface areas, volumes, porosities, etc.

•In the first system, the pores of the Pd nanoparticles are tortuous and ~3 nm in diameter.

•Upon heating the particles *in-situ* to ~200 °C, the beginning of pore collapse was observed. At this point the sample was cooled and tomography was performed. The reconstruction shows that pores migrate together, collapse on each other, and form larger bubbles.

•To study a later stage in pore evolution, the particles were heated to ~600 °C *in-situ*. Larger bubbles were observed in the 2-D TEM images, so the sample was cooled and tomography was performed. These reconstructions show that the tortuous pores have all collapsed into bubbles that are locked *inside* of the nanoparticles. If they are heated to higher temperatures, it is observed that the bubbles eventually escape to the surface, completely destroying all porosity in the material.

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