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Quantitative EDS Analysis of Nanometer-Scale Core/Shell Pd/Rh Structures

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Palladium and its alloys are known to be useful for applications such as catalysis [1], electrocatalysis [2], and hydrogen isotope storage and separation [3, 4]. Increasing the surface area/volume ratio by making Pd alloys nanoporous enhances surface-limited reaction rates, and also provides an escape path for destructive, high-pressure helium bubbles that form during the decay of tritium [5-8]. When Pd is alloyed with a higher melting temperature metal such as Rh, the temperature range over which the nanoporous structure remains morphologically stable is extended [7]. We use a variety of techniques to fabricate nanoporous Pd/Rh alloys, including surfactant templates [6] and the consolidation of dendrimer-encapsulated nanoparticles [9]. It is crucial to understand the spatial distribution of Rh in these structures because of the large effect it has on thermal stability. It is desired for the particle surfaces to be coated with Rh so that the surfaces remain morphologically stable at elevated temperatures.

The microstructure that results from the consolidation of dendrimer-encapsulated particles contains agglomerates of crystalline particles that are approximately 5 nm in diameter. There is a network of pores that surrounds the particles, with diameters that range from a few nm to several tens of nm (Fig. 1). Determining the distribution of Rh presents a difficult challenge because of the overlap of both the Pd and Rh L x-ray lines in EDS, and the delayed-maxima M edges in EELS. In addition, the small size of the individual particles (5 nm diameter) provides very little signal to produce enough counts for quantification. To overcome these challenges, we use multivariate statistical analysis routines [10, 11] to denoise the low-count rate data, followed by multiple-least squares fitting and the Cliff-Lorimer ratio technique [12] to quantify the spatial distribution of Rh. While a conventional 200 kV FEG TEM provides us with enough signal to quantify the average Rh concentration in a given region of the sample, the core/shell structure is not discernible. A 200 kV aberration-corrected STEM with EDS detectors in the pole piece (FEI's ChemiSTEM), on the other hand, provides us with enough x-ray counts to distinguish and quantify the Rh-rich shell and Pd-rich core in these nanoscale materials (Fig. 2).

References:

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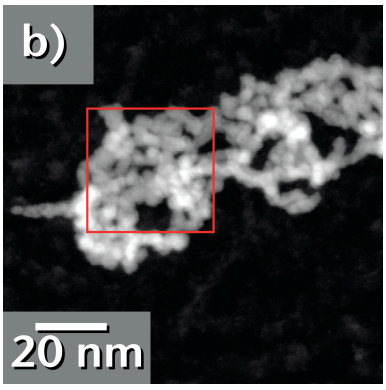
Fig. 1. HAADF STEM image a), showing the overall structure of the consolidated dendrimer-encapsulated nanoparticles. Higher-magnification HAADF image b), and corresponding Rh concentration map c) calculated from an EDS spectrum image collected in the red box of b). Fig. 1. data collected on a JEOL 2010 F operated at 200 kV.



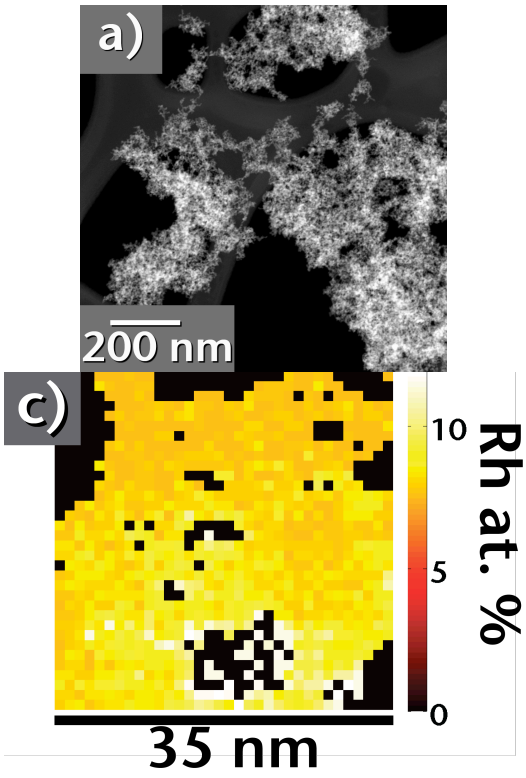


Fig. 2. ADF STEM image a), showing a visible core/shell structure in the Pd/Rh particles. Higher-magnification image b), showing a particle pair that was analyzed using EDS spectrum imaging. Rh concentration map c), calculated with a Cliff-Lorimer k-factor of approximately 1. In c) the Rh-rich shell is visible. Fig. 2. data collected on a probe-corrected FEI Titan operated at 200 kV with ChemiSTEM.