

## Ultra-Small and Monodisperse Pt Nanoparticles Supported on Gamma-Al<sub>2</sub>O<sub>3</sub>

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Metal nanoparticles (NPs) show unusual size-dependent optical, electronic, chemical, and catalytic properties; for example, Au particles on TiO<sub>2</sub> are catalytically active for CO oxidation only when the Au NP is ~3 nm [1]. The novel size effects in heterogeneous catalysis must result from the change of atomic and/or electronic structures of supported metal NPs. Hence, an important goal to understanding and controlling heterogeneous catalysis is the ability to synthesis supported metal nanoparticles of a specific size and shape with a very narrow size distribution. Here we report the results of using forefront chemical synthesis methods to create ultra-small Pt NPs supported on gamma alumina and characterized by high-angle annular dark-field imaging (HAADF, or Z-contrast), high-resolution transmission electron microscopy (HREM) and extended X-ray absorption fine-structure (EXAFS) spectroscopy. The EXAFS measures the ensemble-average structure of the particles within the entire sample, while TEM measures individual Pt NPs. More than 600 individual Pt NPs were analyzed by HAADF to gain statistically meaningful information on the size distribution.

The micellar Pt NPs were encapsulated with PS-PV2P diblock-copolymers and then the organics were removed by treatments with O<sub>2</sub> at selected temperatures, and then reduced in H<sub>2</sub> gas. The Pt NP sizes were controlled by changing the length of the polymer head (P2VP) and by tuning the metal salt to P2VP concentration ratio. The TEM samples were prepared by spreading a drop of Pt/γ-Al<sub>2</sub>O<sub>3</sub> suspension in ethanol onto an ultra-thin C-grid and dried in air. The HAADF and HREM observations were carried out with JEM 2100F S/TEM, operated at 200 kV, and the HREM images were filtered with GIF Tridiem.

Remarkably uniform ultra small Pt NPs were produced by this chemical method. Fig. 1 presents representative HAADF images from two samples of 1 nm or less Pt NPs supported on γ-Al<sub>2</sub>O<sub>3</sub> with different loadings. The size measurements of Pt NPs were based on the full width at half-maximum (FWHM) from the linear intensity-profile across a particle from Z-contrast images. Fig. 2 shows EXAFS measurements of a sample before and after the reduction in H<sub>2</sub> revealing 1nm sized Pt NPs. Fig. 3 is a representative HREM image, which shows the atomic structure of Pt NPs with sizes around 1 nm and in agreement with EXAFS. Both the as prepared and reduced samples show high degree of ordering.

Other heterogeneous catalytic systems will also be synthesized and characterized. The ability to create uniform nanosized metal nanoparticles is necessary for the fundamental understanding and ultimately control of the unusual mesoscopic behavior of nanomaterials, such as heterogeneous catalysis. Complementary characterization techniques, along with theoretical simulations, are essential to correctly understand the atomic and electronic structure of these nanoscale materials.

## References

- [1] M. Valden, X. Lai, and D. W. Goodman, *Science* 281 (5383), 1647 (1998).  
 [2] We acknowledge the Department of Energy-Basic Energy Sciences funding, DE-FG02-03ER15476 and DE-FG02-08ER15995, and NCF at the University of Pittsburgh.

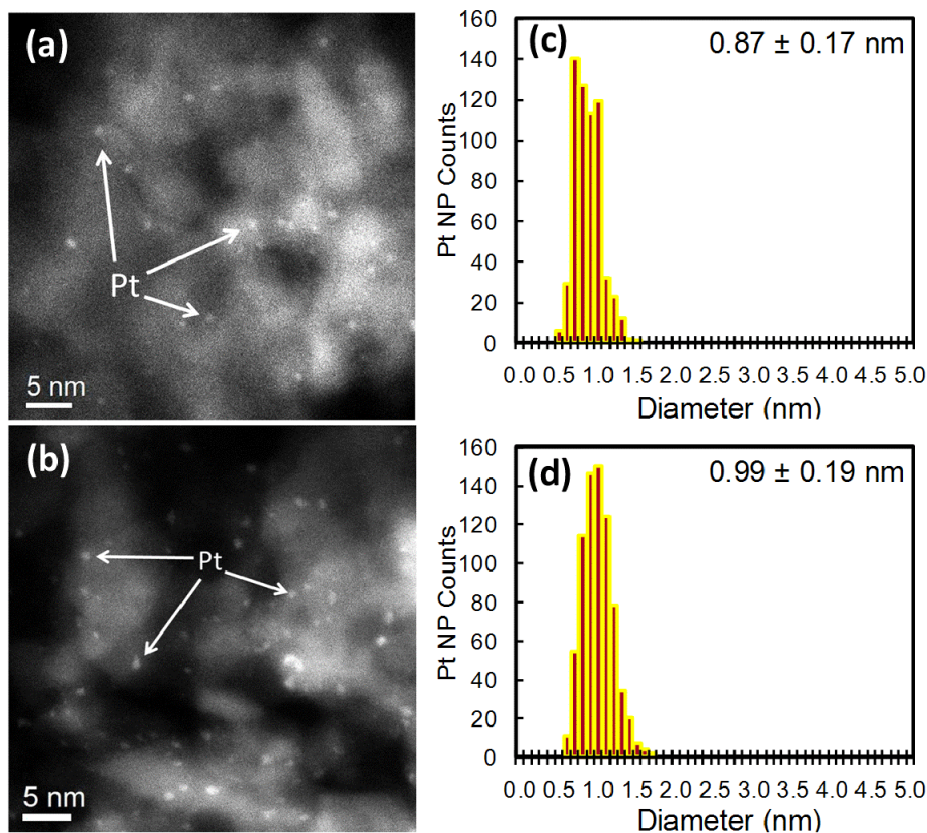


FIG. 1. (a) and (b) Representative HAADF images of Pt NPs on  $\gamma$ - $\text{Al}_2\text{O}_3$  from two samples of different synthesized conditions, and (c) and (d) the histograms for size distribution corresponding to (a) and (b).

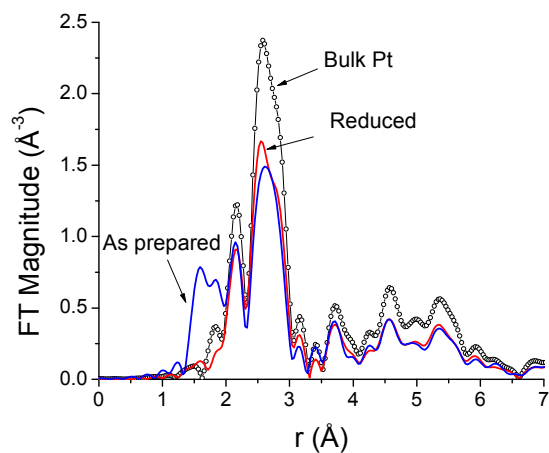


FIG. 2. Fourier transform magnitudes of EXAFS data from the sample as prepared ( $\sim 1$  nm) at room temperature which shows a strong Pt-O peak at low  $r$ , and the same sample reduced in  $\text{H}_2$  at  $375^\circ\text{C}$ . Pt foil data are shown for comparison.

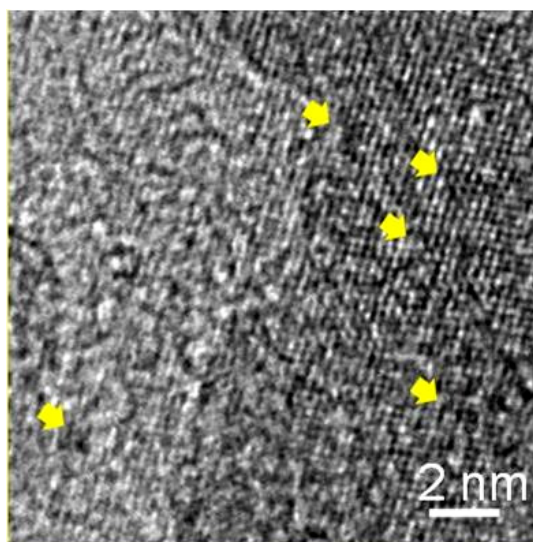


FIG. 3. Representative HREM image, showing  $\sim 1$  nm Pt NPs (some labeled with arrows) on the crystalline  $\gamma$ - $\text{Al}_2\text{O}_3$  support. The Pt NPs adopted none-crystalline structure at sizes of around 1 nm.