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H_2-Driven Crystallization of Supported Pt Nanoparticles Observed with Aberration-Corrected Environmental TEM

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Supported Pt nanoparticles (NPs) are widely used in heterogeneous catalysis, where activity depends sensitively on the particle structure, including crystallinity. We have previously reported that Pt/γ-Al_2O_3 NPs in the 1.1-2.5 nm size regime coexist in both face-centered cubic (fcc) crystalline and disordered states using high-resolution transmission electron microscopy (HRTEM), X-ray absorption spectroscopy (XAS) and first principle calculations [1]. In the present work, we show that the stability of the fcc phase of these <2.5 nm NPs is a strong function of the ambient environment. Pt particles (1.7±0.5 nm) were prepared according to ref [2], and reduced *in situ* utilizing the FEI Titan Environmental TEM with a post-objective 3rd order aberration corrector (300 kV, Cs < 1.5 μm) at the Center for Functional Nanomaterials (CFN) at Brookhaven National Laboratory. Focal series (FS) HRTEM images (2-4 nm defocus) were taken at each site in order to determine crystallinity of individual NPs, as defocus plays a key role in determining a NP's crystallinity [1, 3]. Aberration correction was critical for both size determination of these small particles due to reduction in delocalization, and increasing the number of accessible zone axes at which lattice fringes could be resolved.

Fig. 1 shows histograms of crystalline/disordered NPs as measured by FS-HRTEM. Less than 43% of as-prepared Pt NPs exhibited order for particles <2 nm (Fig. 1a,e). However, particles >2.5 nm were well-faceted crystals with an fcc structure, as shown in Fig 2. The as-received particles were annealed *in situ* at 385 °C in 1 torr H_2 for 30 minutes, and imaged both under these conditions, and after cooling to room temperature (RT) in H_2 (Fig. 3). After annealing, over 78% of NPs exhibited crystalline order (Fig 1b,f), which is consistent with prior findings that can evoke surface facets and promote 3D structures of NPs [4-6]. After annealing, H_2 was pumped out of the column, and the resulting vacuum of 1×10^{-4} torr had no significant effects on the fraction of crystalline order (Fig 1c,g), indicating slow kinetics of hydrogen desorption. After exposure to air at RT for 10 minutes, the degree of crystallinity decreased slightly, implying that a surface Pt-O layer provides the driving force for amorphization.

References

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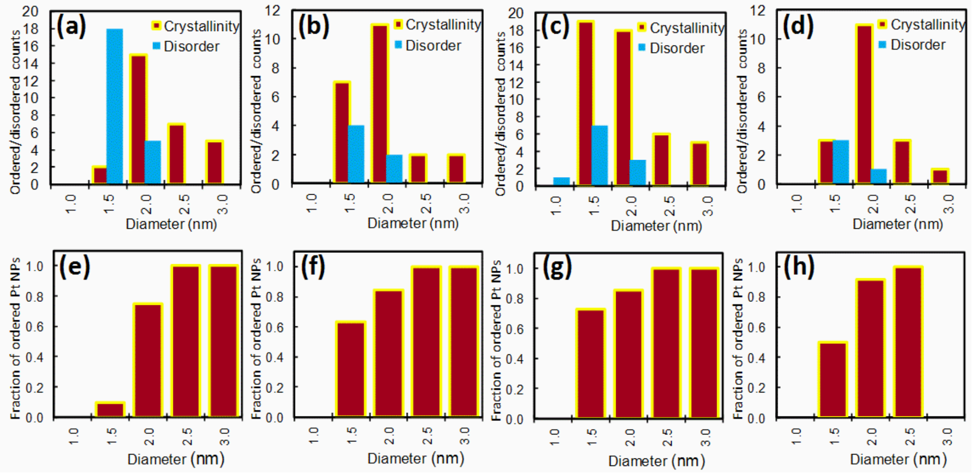

FIG. 1. Histograms of crystalline/disordered NPs at stages of (a) as-prepared, (b) 1 torr H_2 in the ETEM column heated at 385 °C for 30 minutes and then cooled to RT, (c) pumped out H_2 in the ETEM vacuum, and (d) exposed to air for ~10 minutes and then observed in ETEM; (e-h) are distributions of fraction of ordered NPs corresponding to each stages above, respectively.

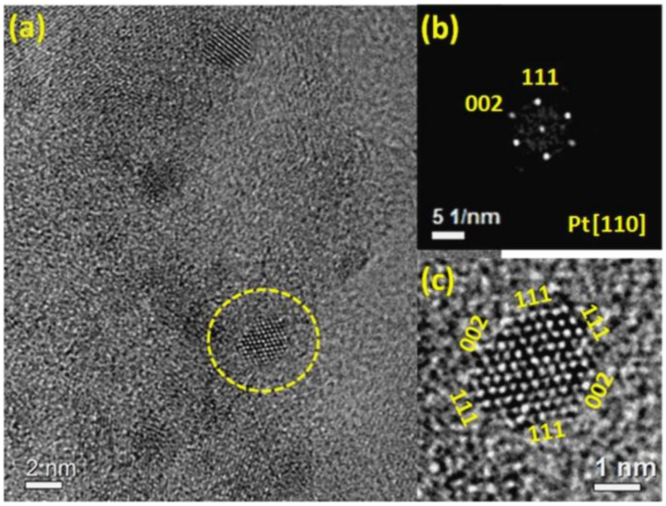

FIG. 2. (a) An HRTEM image of Pt NPs/γ-Al_2O_3 before annealing in H_2, (b) a fast Fourier transform (FFT) of a 2.7-nm crystalline Pt NP, circled in (a), and (c) a magnified image of the particle, showing its clear faceted surfaces.

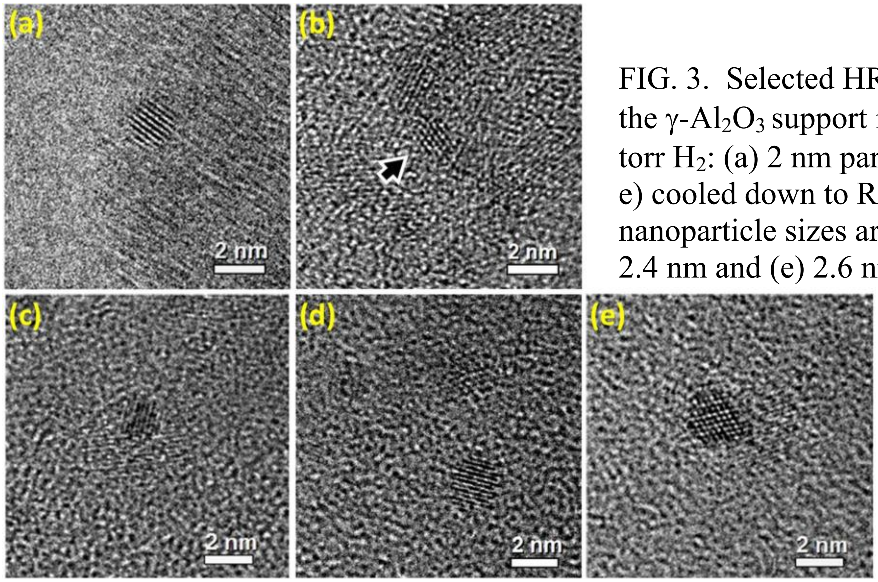

FIG. 3. Selected HRTEM images of Pt NPs on the γ-Al_2O_3 support in the ETEM column of 1-torr H_2: (a) 2 nm particle at 385 °C, and then (b-e) cooled down to RT; the crystalline nanoparticle sizes are (b) 1.2 nm, (c) 1.4 nm, (d) 2.4 nm and (e) 2.6 nm, respectively. Pt NPs tend to be more ordered after annealing in H_2.