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Particle size effect of hydrogen-induced lattice expansion of palladium nanoclusters

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In situ synchrotron x-ray diffraction experiments on bare palladium nanoclusters prepared by inert-gas aggregation and size selected (1.7–6.0 nm) show significant changes in lattice parameter upon hydrogen loading and a narrowing of the miscibility gap, as the cluster size decreases. The results show that the miscibility gap is *open* for all cluster sizes studied, in contrast to previous literature results from surfactant-encapsulated palladium clusters. We interpret these results by showing that the nature of the surface is critical in the hydrogenation behavior of the nanoclusters.

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I. INTRODUCTION

Nanoclusters and nanostructures are of topical interest, with materials often exhibiting different properties from their bulk counterparts. For example, in catalysis, nanoparticles and nanostructured electrodes exhibit significantly increased activity compared to bulk materials. In addition, size effects can cause changes in structural and electronic transitions from discrete to continuous.[1] Not only is this of fundamental scientific interest but also it is important for technological applications: for example, digital devices rely on *discrete* transitions in a material, while sensing devices rely on *continuous* transitions. Metals that form hydride phases represent one class of materials that show size-dependent behavior, where nanosized particles can absorb different concentrations of hydrogen, depending on their size. This makes these materials of interest for hydrogen sensing and storage applications and hence a better understanding of the size effect is important.

Palladium exhibits two distinct hydride phases, denoted as α and β (the latter is sometimes referred to literature as α'), corresponding to low and high concentrations, respectively, of hydrogen atoms incorporated into the Pd crystal structure. In the α phase, the hydrogen atoms behave as a solid solution (randomly occupying interstitial sites) within the face-centered-cubic (fcc) metal lattice, while in the β phase they occupy the octahedral lattice sites, forming a defective rock-salt (NaCl) structure.[2] There is a well-known gap between these two concentration ranges, called the miscibility gap (MG). The existence of the MG is due to the structural transition between the two phases: an energy barrier associated with the incorporation of the hydrogen atoms onto the crystallographic sites and the resultant phase transformation.

The majority of previous studies on palladium nanoclusters exposed to H_2 have focused on measuring the hydrogen fraction (x in PdH_x) as a function of H_2 partial pressure, yielding a pressure-composition (PC) isotherm that was used to determine the MG.[3–6] These studies were performed on Pd clusters synthesized with surfactant shells or encapsulated in polymer matrices and found a significant decrease in the width of the MG with decreasing cluster size. Similar results have been obtained from Monte Carlo calculations.[7] The higher fraction of atoms at the cluster surface has been postulated as the driving force behind this narrowing.[6,8] The exact mechanism is debated: some argue that nanoclusters offer more surface sites for H to occupy and so the α-phase region is expanded to higher concentrations;[6] in contrast a recent publication suggested that the surface did not play a significant role in the increased α-phase solubility.[9] However, PC isotherm studies do not measure the related structural change (α to β transition) during hydrogenation. Previous *in situ* x-ray diffraction (XRD) studies on Pd clusters while exposed to H_2 gas have only been reported for clusters with surfactant shells,[10] encapsulated in polymer matrices[4,5] or on nanograined Pd polycrystalline samples:[11] a significant decrease in the MG with decreasing cluster size was observed and complete closure below ~3 nm.[12]

It is well known that surface effects play an important role in the thermodynamics of nanoparticles.[13] As the α to β transition involves an expansion of the lattice, the corresponding change in surface energy of the particle will lead to a change in the equilibrium between these phases. This effect is significant in nanometer-sized particles. However, it is not known whether this effect in isolation should cause a narrowing or widening of the MG, as it is possible to show that this depends sensitively on the relationship between lattice strain and H loading.[14] Indeed, this uncertainty is compounded by the fact that the surface will become passivated to H absorption as it is exposed to increasing H_2 partial pressures, reducing the effects of the surface tension as the pressure is increased. Thus one cannot say *a priori* if there will be a widening or a narrowing of the MG as particle size decreases.

We report *in situ* synchrotron x-ray diffraction measurements on naked Pd nanoclusters prepared without surfactant shells and compare these to previous literature results on surfactant-encapsulated clusters. The results demonstrate that the naked clusters exhibit significant changes in lattice parameter and a size-dependent narrowing of the miscibility gap, and this dependence is different for naked versus surfactant-encapsulated clusters. Extrapolation of the data suggests that for naked clusters the MG stays open for all finite cluster sizes.

II. EXPERIMENTAL

Palladium nanoclusters were deposited onto Si wafers (with native Si oxide) using an inert-gas aggregation technique described in Ref. 15. Controlling the source conditions varies the cluster size. The size distribution was restricted further by using a mass filter.[16] For this work, three samples were investigated, with mean sizes of 6.1, 3.0, and 1.7 nm. These had approximately Gaussian size distributions with full widths at half maximum (FWHMs) of 0.7, 0.3, and 1.1 nm, respectively (the mass filter could not be used for the smallest clusters due to the low measured flux). In each case, 0.6 nanocluster monolayers[17] were deposited on to the surface. Synchrotron x-ray diffraction experiments were conducted in grazing incidence geometry using beam line 12-ID-B at the Advanced Photon Source at Argonne National Laboratory using an x-ray energy of 24 keV. The sample was mounted inside an environmental chamber that allows the controlled introduction of H_2 gas up to partial pressures of 96 Torr.[18]

There is no empirical evidence that for the system studied here the Pd nanoclusters react with the substrate; we see no indication of Pd silicide phases. The clusters are produced by deposition onto an unreactive surface (Si wafer with native oxide) at room temperature, so reaction is unlikely. The initial surfaces are likely to be oxidized due to exposure to air, but for Pd this is only one atomic monolayer[19] and is removed in the initial exposure to H_2.[12] In addition, the clusters are not expected to be significantly a spherical as a result of impacting the substrate (which may affect how the surfaces respond to the uptake of H_2): the in-plane and out-of-plane grain sizes as determined from XRD are the same.

After mounting each sample, the chamber was purged with argon for 1 h. The hydrogen pressure was then increased in a stepwise fashion, and a diffraction pattern recorded after waiting 10–15 min to allow the system to equilibrate. For several pressure steps, a series of quick scans was taken across a single peak to monitor any time-dependent change. No time dependence was observed, indicating that the kinetics are faster than the scan rate (~1 min). All measurements were performed at room temperature.

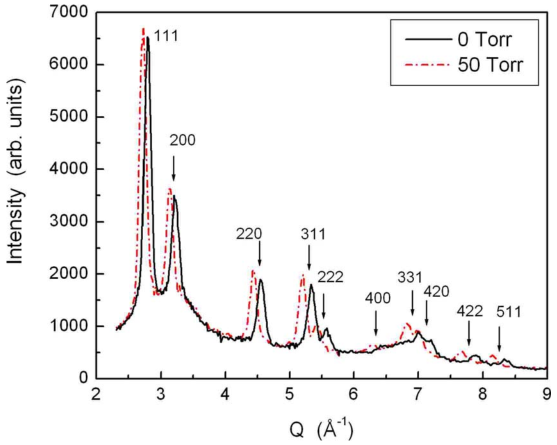

FIG. 1. (Color online) X-ray diffraction patterns recorded at 0 and 50 Torr hydrogen pressures for the 6.1 nm diameter cluster sample. The peaks have been indexed to the fcc structure.

III. RESULTS AND DISCUSSION

Figure 1 shows typical x-ray diffraction patterns for the 6.1 nm cluster sample recorded at H_2 pressures of 0 and 50 Torr (the maximum used for this sample). The peaks are labeled using the indices associated with an fcc structure. While Pd clusters have the ability to form stable nonbulk structures such as icosahedra and decahedra, which have differing size effects on their lattice parameters,[10,20] there is no conclusive evidence for the presence of alternative phases in any of the samples studied.

The shift of peak positions to lower Q with the introduction of H_2 indicates an expansion of the lattice consistent with the formation of the β-hydride phase. Figure 2(a) shows the data and fits to the (111) peak for the 6.1 nm clusters in the α $[p(H_2)=0]$ and β $[p(H_2)=50\ \text{Torr}]$ phase regions and

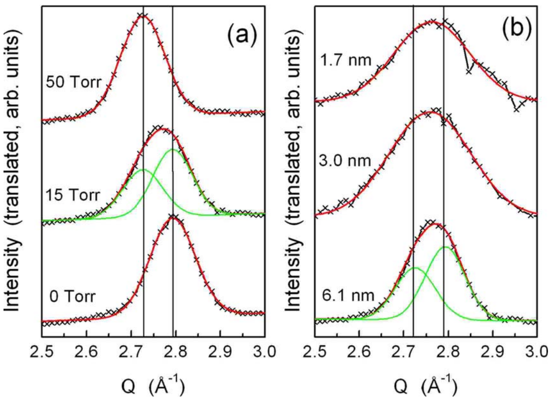

FIG. 2. (Color online) (a) Raw data (black points) and fits (red/gray thick lines) for 6.1 nm cluster (111) peak at pressures corresponding to the α phase only (0 Torr), β phase only (50 Torr), and in the miscibility gap (15 Torr). The 15 Torr fit is comprised of two peaks, as shown (green/light gray thin lines). The positions corresponding to the two peaks are shown by the vertical black lines. (b) Raw data (black points) and fits (red/gray thick lines) for the (111) peak at pressures within the miscibility gap. Only the 6.1 nm data can be fitted with two peaks (green/light gray thin lines). The vertical lines show the position of these two peaks.

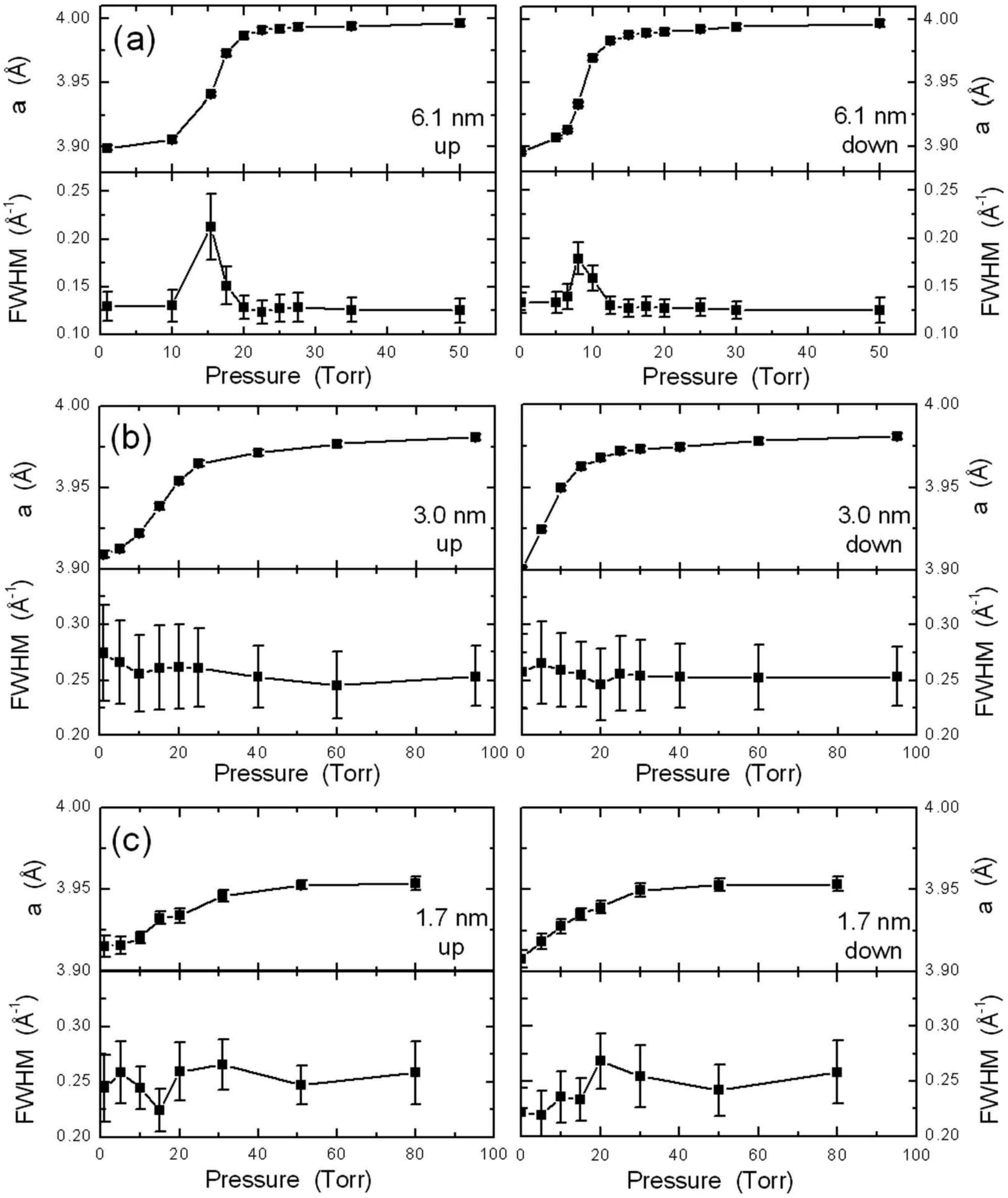

FIG. 3. FWHMs and lattice parameters for (a) 6.1, (b) 3.0, and (c) 1.7 nm clusters upon increasing (left) and decreasing (right) the hydrogen pressure.

for an intermediate concentration [at $p(H_2)=15$ Torr] where the peak is broadened and asymmetric, indicating the presence of two phases (fitted with two peaks, thin lines). We describe this region as the "MG regime," i.e., H_2 pressures intermediate between pure α and pure β phases for the respective cluster sizes.

Figure 2(b) shows data and fits for the three samples in the MG regime. For the largest clusters studied (6.1 nm) there are two peaks (see fitted curves), corresponding to the two distinct phases (as observed in other studies[11]), while for the smaller clusters (1.7 and 3.0 nm) we observe one peak that simply shifts with decreasing cluster size. This is reflected in Fig. 3, which shows the average FWHM for the measurable peaks fitted with a single peak function and how these correlate with the observed shifts in the lattice parameter (determined from the peak position). In the 6.1 nm data the inadequacies of fitting the data with a single peak in the transition regions can be clearly seen as the FWHM increases and then comes back to its original value. For the 3.0 and 1.7 nm clusters, no change in the FWHM is observed within the error bars. In these two samples, the peak width (broadened due to the small crystallite size) is greater than the lattice-parameter change and so two peaks cannot be conclusively resolved. Figure 4 shows the apparent lattice parameter (the true lattice parameter where there is one phase present and the volume average where there are two phases in the MG regime) for the three samples, plotted against the H_2 partial pressure.

From the data for the 6.1 nm clusters in Fig. 4, one can extract the lattice parameters corresponding to the maximum H_2 pressure at which the α phase is observed on the upward leg and the minimum H_2 pressure for the β phase on the

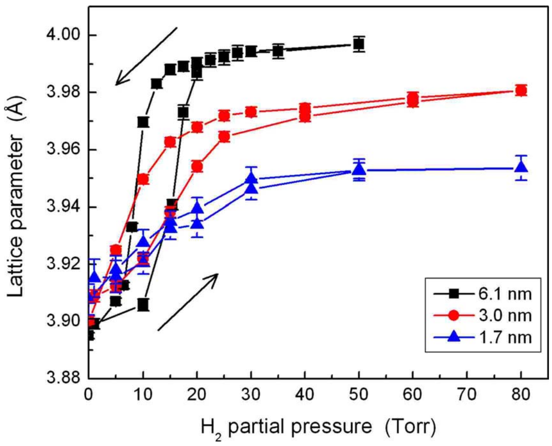

FIG. 4. (Color online) Lattice parameters obtained from fitting the peak positions from x-ray diffraction patterns for the three cluster diameters studied as a function of hydrogen pressure. The arrows indicate the direction of the hydrogen pressure change.

downward leg, henceforth denoted as $a(\alpha_{\max})$ and $a(\beta_{\min})$, respectively; these define the boundaries of the MG. The extent of the MG is therefore the difference between the concentration values $x=\alpha_{\max}$ and $x=\beta_{\min}$ in PdH_x. In the XRD data, $a(\alpha_{\max})$ and $a(\beta_{\min})$ correspond to the extremes of the region where there is coexistence of the two phases and these are seen as two peaks [see Fig. 2(a)]. However for the smallest clusters two peaks cannot be resolved and a different approach is required. Based on the behavior of the larger clusters and the bulk system where two peaks are seen,[11] we determine $a(\alpha_{\max})$ and $a(\beta_{\min})$ from the opening and closing of the hysteresis loops in Fig. 4. Hysteresis in the lattice parameter of clusters during sorption and desorption of hydrogen provides evidence that the MG is still open,[21] even when no plateaulike behavior is evident.[21,22] The $a(\alpha_{\max})$ and $a(\beta_{\min})$ values are shown as a function of particle size along with experimental bulk and nanograined values from in Fig. 5 of Ref. 11. Also shown are values from clusters fabricated with a surfactant shell from Ref. 12.

Figure 5 demonstrates that cluster size dramatically affects the MG, which is related to the difference between $a(\alpha_{\max})$ and $a(\beta_{\min})$. The values of $a(\alpha_{\max})$ and $a(\beta_{\min})$ from the current work fall on two lines (blue solid for $\beta_{\min}$ and black dotted for $\alpha_{\max}$) that extrapolate to intersect at a cluster diameter of zero. (At larger sizes, the trends will be nonlinear, as they must approach the bulk smoothly.) Data (triangles) for a nanograined sample with ~8 nm particles[11] yield values that also fall on these lines. It has been shown previously that the change in lattice parameter is approximately linear with H concentration.[23] However, it is not clear that this relation can be applied to clusters. Therefore we are reluctant to infer the absolute concentrations $\alpha_{\max}$ and $\beta_{\min}$ from these data. Lattice parameters for surfactant-encapsulated clusters[12] are also shown in Fig. 5 as the open circles $[a(\alpha_{\max})]$ and closed circles $[a(\beta_{\min})]$. The $a(\beta_{\min})$ values follow a similar trend compared to the naked clusters, falling along the same (solid) line. However the $a(\alpha_{\max})$ values are significantly different (red dashed-dotted line).

Our data in Fig. 5 show that naked clusters have a nonzero MG for all cluster sizes (also evidenced by the open hysteresis loops[21] in Fig. 4). In previous work on clusters with surfactant shells, it was argued that the gap closes for clusters smaller than 3 nm.[12] However the data in Ref. 12 are scattered for both $a(\alpha_{\max})$ and $a(\beta_{\min})$ and the raw data used to obtain $a(\alpha_{\max})$ are ambiguous at the lowest H_2 partial pressures, as there is no plateau. Nevertheless, there is a significant difference between the $a(\alpha_{\max})$ values for naked and surfactant-covered clusters. The only difference between these clusters is the nature of the surface. Therefore we conclude that the nature of the surface affects the behavior of the α phase, but any surface effects are unimportant once the clusters are in the β phase.

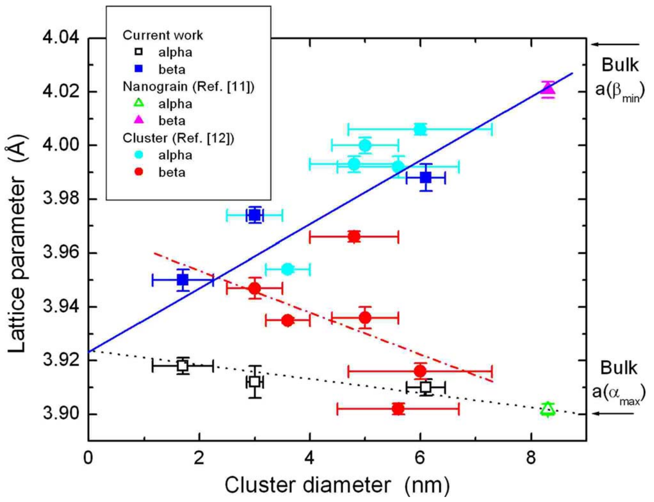

FIG. 5. (Color online) Lattice parameters corresponding to $\alpha_{\max}$ and $\beta_{\min}$ for the three samples under study, compared with bulk and nanograined Pd (Ref. 11) and clusters with surfactant shells (Ref. 12). The solid and dotted trend lines are given as guides.

The results illustrate how the nature of the cluster surfaces is important. Naked clusters do not show complete closure of the MG, while surfactant-encapsulated clusters do.[12] This is solely due to the difference in the behavior of $\alpha_{\max}$ (red dotted-dashed and black dotted lines in Fig. 5), as the $\beta_{\min}$ behavior (solid blue line in Fig. 5) is the same. The α-phase solubility increase in clusters has been attributed to the availability of surface sites which are easy for H to occupy.[6] In comparing naked clusters (on a weakly interacting substrate) with surfactant-encapsulated clusters, one would expect the surface layer of atoms in the surfactant-encapsulated case to have slightly weaker bonds to the cluster core, therefore allowing the ingress of more H into the subsurface atomic layers. Indeed, between different types of surfactants there are different H_2 partial pressures required to form the hydride phase.[4] Naked clusters would have a stronger bond between the surface and subsurface layers and hence require higher H_2 partial pressures to form the β phase. While both naked and surfactant-encapsulated clusters will have a modified surface energy upon exposure to H_2, this effect will be different in both cases as the dissociated surface H on the naked clusters is much smaller and more mobile than the function groups of the surfactant molecules. A recent publication[9] suggested that the α-phase behavior arises from the cluster volume, not the surface. However, this study was performed on *epitaxial* particles, i.e., with strong cluster-substrate interaction, which will cause significant lattice strain in the cluster. In that case, the internal H pressure is not the driving force behind the formation of the α phase.

Interestingly, Fig. 4 shows that at zero H_2 partial pressure the measured lattice parameter of the particles *increases* as particle size decreases. This is also reflected in Fig. 5 where the α-phase lattice parameter increases for decreasing sizes. This is contrary to what is usually found in nanoparticles where surface tension leads to a *decrease* of the mean lattice parameter as the particle size decreases.[24] A lattice contraction with decreasing particle size has previously been observed in Pd,[25] where it was noted that an increase in lattice parameter was usually seen. Several possibilities for lattice expansion with decreasing particle size were given: pseudomorphism (primarily due to substrate epitaxy), the presence of impurities within the particles, the presence of a surface oxide, or a structural change.[25] The potential magnitude of these effects is difficult to quantify. If we consider, for example, a structural change (e.g., fcc to icosahedral), for the same diameter particle the icosahedral structure does indeed have a larger average “lattice parameter” than the fcc structure; however over the size range measured (6.1–1.7 nm) we would still expect a decrease from theory.[14] In our studies, it is most likely that the lattice expansion effect seen at zero H_2 partial pressure as the cluster size decreases is due to the presence of a residual surface oxide.

IV. SUMMARY

We have shown that there is a narrowing, but no closure, of the miscibility gap in naked Pd-H nanoclusters as the cluster size is decreased. That is, the transition remains discrete for all particle sizes. This is in contrast to previous measurements of clusters with surfactant shells and encapsulated in polymer matrices. We have shown that the narrowing is due to effects at both ends of the miscibility gap: (i) the existence of the α phase at higher hydrogen concentrations and (ii) the existence of the β phase at lower hydrogen concentrations as the cluster size decreases. The dependence of $a(\beta_{\min})$ on cluster size is the same for naked clusters and those with surfactants. The increase in $a(\alpha_{\max})$ is small but is different for clusters with and without surfactants. We attribute this behavior to the differences in the nature of the cluster surfaces; this shows that the nanocluster surface has an important effect on the hydrogenation behavior.

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