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EXAFS Studies of Palladium Nanoparticles: Size Control and Hydrogenation

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Abstract. We synthesized several samples of thiol-stabilized Pd nanoparticles by controlling their size with the palladium/thiol ratio from 5:1 to 1:3. Size dependence on the Pd/thiol ratio was verified by comparing the Pd-S and Pd-Pd coordination numbers. The average size of free-standing nanoparticles decreased as the thiol concentration increased and stabilized at the 1:2 value of palladium/thiol ratio. In addition to the free-standing nanoparticles, we analyzed their thin films by depositing them as monolayers on Kapton film using Langmuir-Blodgett technique. We obtained that the structure of the nanoparticles was preserved, within the accuracy of the EXAFS measurement, after preparing Langmuir films. We also studied the effect of hydrogenation on the both type of the nanoparticles (the free standing ones and those in the monolayers). In both cases, exposure to 4 atm H_2 pressure resulted in the elongation of the average Pd-Pd distance. The larger change (0.06±0.03 Å, relative to the non-hydrogenated films) was observed in the smaller clusters (with 1:1 Pd thiol ratio), and the smaller change (0.03±0.01 Å) – in the larger clusters (with 3:1 ratio). Such bond length expansion is attributed to the defects caused by H_2 adsorption.

Keywords: EXAFS, nanoparticles, hydrogenation.
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INTRODUCTION

Thiol-stabilized palladium nanoparticles have tunable electric, magnetic and structural properties which makes them important for catalysis and hydrogen storage. Single-sized palladium clusters have demonstrated enhanced solubility of hydrogen relative to the bulk [1]. In metal-hydrogen alloys, hydrogen absorption occurs by hydrogen atoms occupying interstitial sites, which causes metal atoms to be displaced from their ideal sites as studied by X-ray diffraction (XRD) [2]. Those experiments demonstrated Pd-Pd length expansion in hydrogenated Pd nanoclusters. However, the size effect of hydrogen absorption on the Pd nanocluster lattice has not been studied systematically as a function of the cluster size and structure. For example, in the XRD study [2] the larger clusters were proposed to be cubic, while the smaller ones – icosahedral. Furthermore, XRD measurements in small clusters are not accurate for their bond length determination – and it is the Pd-Pd bond length which is most sensitive to hydrogen-induced structural defects. This paper presents several proof-of-the-principle experiments where we investigate changes in the Pd-Pd bond length, resulting from hydrogen absorption by Pd nanoclusters, using EXAFS. We used alkanethiols as surfactants in order to stabilize the nanoparticles from growth. Their size was controlled by varying the palladium/thiol ratio from 5:1 to 1:3. In addition to the free-standing nanoparticles, we analyzed their size and structure before and after hydrogenation in thin films by depositing the nanoclusters as monolayers on Kapton film using Langmuir-Blodgett technique.

EXPERIMENTAL DETAILS

This section describes details of the nanoparticle synthesis, Langmuir film depositions, hydrogenation and EXAFS measurements.

Nanoparticle Synthesis

The dodecanethiolate palladium nanoparticles (Pd-C12) were synthesized using a Brust method [3] In this method, an aqueous solution of K_2PdCl_4 (0.5 mmol in 20 mL H_2O) was mixed with a solution of

tetraoctylammonium bromide in toluene (2.4 mmol in 20 mL toluene). The two-phase mixture was vigorously stirred until all the $PdCl_4^{2-}$ was transferred into the organic layer. Different amounts of dodecanethiols were then added, to prepare samples with for different Pd/thiol ratios, from 5:1 to 1:3. A freshly prepared aqueous solution of sodium borohydride (6 mmol in 10 mL water) was added at a rate of 2 mL/min under vigorous stirring, the organic phase changed color from burnt orange to dark brown within a few minutes. After being stirred for 3 hours the organic phase was separated, evaporated to 5 mL in a rotary evaporator and mixed with 160 mL ethanol to remove excess thiol. The mixture was centrifuged to get the black precipitate, which was washed with ethanol for four times and dried in a vacuum desiccator.

Langmuir Film Deposition

Langmuir monolayers of the Pd-C12 particles were prepared using the Langmuir-Blodgett (LB) technique. The nanoparticles were mixed with toluene and spread on the air-water interface in a LB trough, immediately forming ordered islands on the water surface. They were then deposited on Kapton films when the surface pressure reached about 7.8 mN/m. A stack of 750 Langmuir films was used to prepare a specimen for hydrogen absorption studies and for EXAFS measurements.

Hydrogenation

Pd nanoparticles (free standing, on adhesive tapes, and the monolayer-deposited using LB method) were exposed to 4 atm of hydrogen for 30 min inside the autoclave at room temperature. EXAFS studies were performed within several hours after hydrogenation.

EXAFS Measurements

EXAFS measurements were performed at the Pd K-edge using X11A beamline at the NSLS, Brookhaven National Laboratory. Free-standing nanoparticles were analyzed in transmission mode, and the Langmuir films – in flurescence mode, using a five-grid Lytle detector.

EXAFS DATA ANALYSIS

EXAFS data (Figs. 1, 2) were processed by IFEFFIT [4]. Fig. 1 demonstrates that the Pd-S contribution decreases and Pd-Pd contribution increases as the As Pd/thiol ratio increases from 1:3 to 5:1. These changes are consistent with the progressive

increase of the average Pd nanoparticle size as the Pd/thiol ratio increases, due to the progressively decreasing surface to volume ratio of Pd atoms.
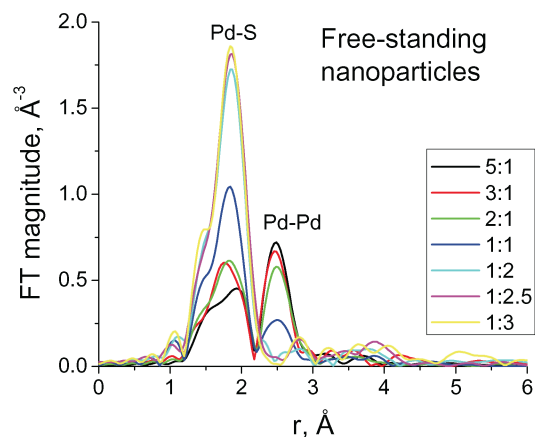

FIGURE 1. Fourier transform magnitudes of the EXAFS data in free-standing nanoparticles for different values of Pd/thiol ratio.
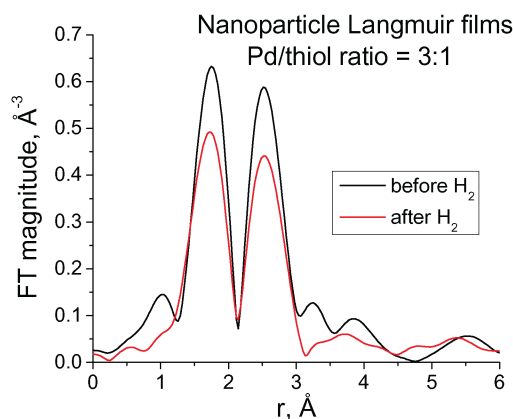

FIGURE 2. Fourier transform magnitudes of the EXAFS data in nanoparticles deposited as Langmuir films before and after hydrogenation.

Theoretical Pd-S and Pd-Pd nearest neighbor paths were simulated by FEFF6 [5] for the bulk standards. The fits were performed in r-space, using k^2-weighting and the 2-14 $Å^{-1}$ k-range. The ΔE_0 correction, the coordination numbers, distances and Debye-Waller factors of the Pd-S and Pd-Pd bonds were varied in the fits.

RESULTS

The representative plot of the data and the FEFF6 fit (for the 3:1 ratio) is shown in Fig. 3. Numerical

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results for the coordination numbers of the free-standing and Langmuir film nanoparticles are reported in Table 1. Pd-S and Pd-Pd 1NN distances obtained before and after hydrogenation of the free-standing (Pd/thiol ratio of 1:1) and Langmuir film (3:1) are reported in Table 2.
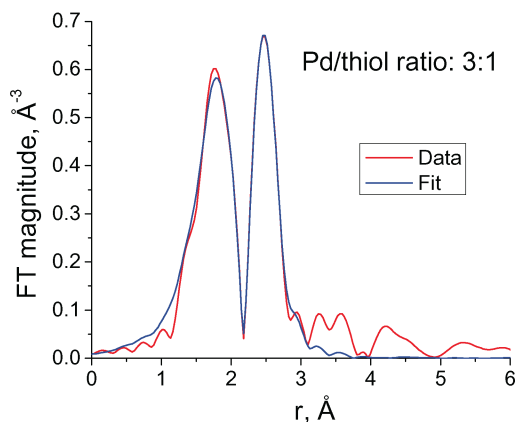

FIGURE 3. Fourier transform magnitudes of the EXAFS data and FEFF6 fit in free-standing nanoparticles at the 3:1 Pd/thiol ratio.

TABLE 1. Coordination numbers of Pd-S and Pd-Pd bonds obtained by EXAFS analysis of free-standing nanoparticles

Pd/thiol ratio	N(Pd-S)	N(Pd-Pd)
5:1	1.5(6)	5.3(8)
3:1	1.7(2)	5.0(4)
3:1(LB)	1.1(4)	4.5(1.0)
2:1	2.0(3)	4.0(6)
1:1	2.7(4)	2.1(9)
1:2	4.4(3)	-
1:2.5	4.4(5)	-
1:3	4.4(5)	-

TABLE 2. Pd-S and Pd-Pd 1NN distances obtained by EXAFS analysis of free-standing and Langmuir film-deposited nanoparticles before and after hydrogenation

Pd/thiol ratio	R_{Pd-S}(Å)	R_{Pd-Pd}(Å)
Pd foil	-	2.751(1)
1:1 before H_2	2.32(1)	2.74(2)
1:1 after H_2	**2.31(1)**	**2.80(3)**
3:1 (LB) before H_2	2.29(2)	2.753(9)
3:1 (LB) after H_2	**2.27(3)**	**2.78(1)**

Our results demonstrate that the Pd-S coordination numbers increase monotonically and stabilize at the 1:2 value of Pd/thiol ratio as the thiol concentration increased. Thus, their behavior is similar to that observed previously by EXAFS in thiol stabilized Au nanoparticles [6]. In such systems, the stabilization at 1:1 value of Au/thiol ratio was attributed to the preferential formation of low-molecular-weight thiol complexes v. Au/thiol complexes due to the increased effect of thiol-thiol repulsion at high thiol concentration.

While the average particle size changes predictably with Pd/thiol ratio, the distribution of the sizes is not narrow. Indeed, the smallest 1NN Pd-Pd coordination numbers in regular polyhedral clusters are in the 13-atom cuboctahedron (5.5) and 13-atom icosahedron (6.5). In our clusters (Table 1), the largest coordination numbers (5.3±0.8) is measured for the clusters with 5:1 Pd/thiol ratio. Thus, these clusters are either monodispersed Pd13 clusters, or there is a range of compositions, with clusters of all sizes present, from large, several nm in diameter, to the low molecular weight Pd-thiol complexes. We have also considered a model of monodispersed and large Pd particles which have reduced Pd-Pd coordination numbers due to mutiple twinnings. However, such possibility does not explain too large the Pd-S coordination numbers that we observed. Thus, we believe, results reported in Table 1 can be explained by the relatively broad particle size distribution. This conclusion was independently verified by our TEM measurements.

Results of the hydrogenation measurements for free-standing nanoparticles and those in the Langmuir monolayers demonstrated that the exposure to 4 atm H_2 pressure resulted in the elongation of the average 1NN Pd-Pd distance. The larger change (0.06±0.03 Å, relative to the non-hydrogenated films) was observed in the smaller clusters (with 1:1 Pd/thiol ratio), and the smaller change (0.03±0.01 Å) – in the larger clusters (with the 3:1 ratio). Such bond length expansion is attributed to the lattice defects caused by H_2 adsorption.

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