

An XAFS Study on the Local Structure of Molecularly Capped Gold-Palladium Nanoparticles

F. Liu and P. Zhang

Department of Chemistry, Dalhousie University

27

PRINCIPAL CONTACT:

P. Zhang

Principal Investigator

Dalhousie University

E-mail: peng.zhang@dal.ca

Introduction

Bimetallic Au-Pd nanoparticles (NPs) of varied Au concentrations, (i.e. 25%, 50% and 75% Au), have been prepared using weakly capping molecules (amine and bromide surfactants). TEM results show that the average particle sizes of the NPs are all in the range of 3-3.5 nm. Analysis of the average coordination number and Au-Au bond distance obtained from Au L_3 -edge XAFS indicates that the 25% Au NPs have a cluster-on-cluster structure

whereas both the 50% and 75% Au NPs have enriched core-shell structures.

Science

Research on the structure and properties of metal nanoparticles (NPs) has attracted a great deal of interest because of their promising applications in catalysis, optoelectronics, bio-detectors, etc. [1]. In order to better control the properties of metal NPs, the addition of a second metal is often considered as an excellent choice. In this context, control of the local structure of the bimetallic NPs is of critical importance in view of tailoring their chemical and physical properties towards various technological applications. We have recently developed a preparative method using a mixture of two kinds of capping molecules in the synthesis of bimetallic NPs. The use of two kinds of capping molecules instead of one has been proven to offer more flexibility in the control of the local structure of the NPs. In this report, we present the results on the local structure of some of these NPs from Au L_3 -edge XAFS measurements conducted at the HXMA beamline 06ID-1.

Discussion

The NPs were prepared by reducing Au and/or Pd compounds of desired ratio (3:1, 1:1 and 1:3) in the presence of a mixture of dodecylamine (DDA) and tetraoctylphosphonium bromide (TOPB) capping molecules in a toluene solution. The molar ratio of metal:DDA:TOPB was maintained at 1:12:3 for all the NPs. The average sizes measured by transmission electron microscope (TEM) are 8.0 nm for 100% Au, 3.2 nm for 75% Au, 3.5 nm for 50% Au and 3.3 nm for 25% Au. Figure 1 shows representative TEM images of 100% Au NPs and 50% Au NPs. It can be seen that the bimetallic NPs are considerably smaller than the 100% Au NPs. This observation suggests the existence of strong Au-Pd interaction in the bimetallic samples.

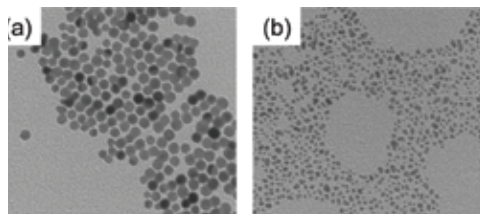


Figure 1. TEM of 100% Au NPs (a) and 50% Au NPs capped with a mixture of DDA and TOPB.

Figure 2 shows the k^3 -weighted XAFS of the NPs with various Au concentration and bulk Au. As the Au concentration decreases, it is evident that the XAFS oscillation patterns differ gradually from that of bulk Au. This observation indicates that, as the Au concentration in the NPs decreases, the average number of Pd neighbor atoms increases, resulting in more intense Au-Pd interaction in the NPs.

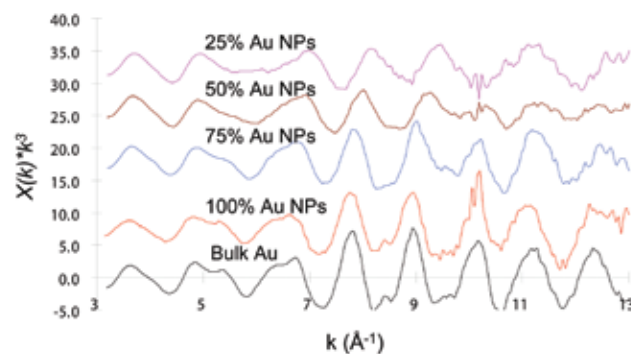


Figure 2. k^3 -weighted Au L_3 -edge XAFS data of NPs with various Au concentration and bulk Au.

Figure 3 shows the XAFS radial distribution function obtained from the k -space data presented in Figure 2. Fittings of the XAFS were conducted using the FEFF 8 program [2] in the R-space for the first shell (1.7-3.3 Å). A 50% alloy cluster consisting of 135 atoms was constructed and used to generate the theoretical phase and amplitude functions from FEFF 8. Table 1 presents the Au-Au and Au-Pd coordination numbers and bond distance. The 25% Au NPs were found to have a very small coordination number for the like neighbour atoms ($N_{\text{Au-Au}}$) whereas the 50% and 75% Au NPs show much greater $N_{\text{Au-Au}}$ values. Meanwhile, the $N_{\text{Au-Pd}}$ values decrease as the Au concentration increases. The ratio of $N_{\text{Au-Au}}$ to $N_{\text{Au-Pd}}$ can be used to judge whether or not homogeneous alloying structure is formed. If $N_{\text{Au-Au}}/N_{\text{Au-Pd}}$ is the same as the molar ratio of Au to Pd in the NPs, it indicates the existence of homogeneous alloy. The data in Table 1 indicate that none of the Au-Pd NPs have homogeneous alloying structure. The uncertainty is about 0.02 Å for R and 15% for N.

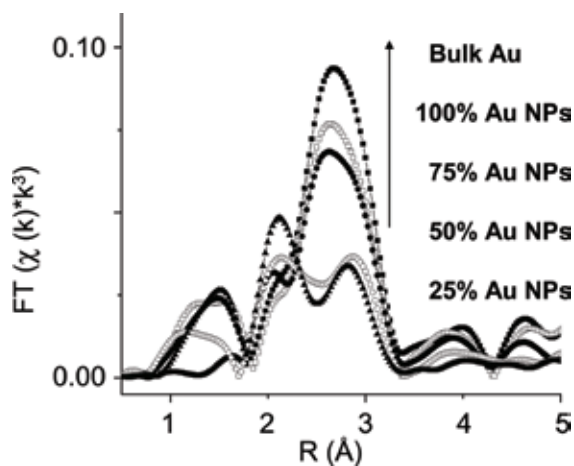


Figure 3. XAFS radial distribution function of Au NPs with various Au concentration and bulk Au obtained from k -space data in the range of $3\text{-}13\text{\AA}^{-1}$.

Table 1. XAFS fitting results of Au-Pd NPs.

Sample	M-M Bond	NAu-Au	R (Å)	M-M Bond	NAu-Pd	R (Å)
25%Au NPs	Au-Au	3.32	2.78	Au-Pd	2.54	2.78
50%Au NPs	Au-Au	8.21	2.81	Au-Pd	2.06	2.80
75%Au NPs	Au-Au	10.21	2.84	Au-Pd	1.42	2.86

To better understand the relationship between the coordination number and the local structure of fcc metal clusters, we construct three magic number clusters with representative average coordination numbers, shown in Figure 4. The coordination numbers for 13-, 55- and 309-atom clusters were calculated to be 5.5, 7.9 and 10.1, respectively. [3]. Based on this information, we proposed that the 50% and 75% Au NPs should have an enriched Au core-Pd shell structure. The 50% Au NPs should have a small Au core whereas the Au core of 75% Au NPs should be much bigger. The very small value of NAu-Au is indicative of very small Au clusters (less than 13 atoms) located on the surface of a Pd core.

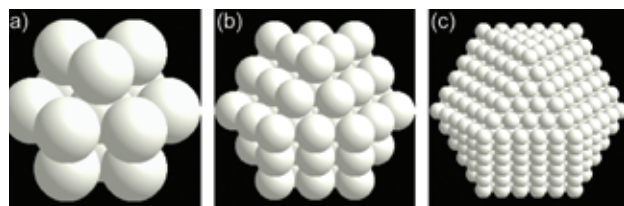


Figure 4. Models of magic-number clusters consisting of 13 (a), 55 (b) and 309 (c) atoms. The average coordination numbers for these clusters are 5.5, 7.9 and 10.1, respectively.

Conclusion

Au L_3 -edge XAFS has been used to study the local structure of molecularly capped Au-Pd NPs with various Au concentrations. Structural models of the bimetallic NPs were proposed based on the XAFS data. These results indicate that the local structures of these bimetallic NPs are dependent on the concentration of Au in the NPs. Use of 50% and above of Au lead to an enriched core-shell structure. When the Au concentration is low relative to that of Pd (e.g. 25% Au), a cluster-on-cluster structure is resulted.

Acknowledgements

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References

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