

Imaging Au-Pd Nanoparticles with the Aberration-Corrected STEM/TEM

M. José-Yacamán,* S. Mejía-Rosales,** E. Pérez-Tijerina,** D. A. Blom*** and L. F. Allard***

*Texas Materials Institute and Chemical Engineering. Dept., UT-Austin, Austin, Texas, USA 78712

**Facultad de Ciencias Físico-Matemáticas, Univ. Autónoma de Nuevo León, San Nicolás de los Garza, N.L., México 66450 3

***Materials Science and Technology Division, ORNL, Oak Ridge, TN 37831-6064, USA

The understanding of the way in which matter organizes into clusters with thousands of atoms is one of the most important and challenging problems in catalysis and nanotechnology. When two species of atoms with different radii are involved, the expected packing will be more complicated and a richer spectrum of structures is anticipated, ranging from quasicrystals and amorphous crystals to well-ordered superlattices and core-shell structures [1]. This plethora of structures has been predicted by theoretical calculations and observed by a number of authors [2], and it is one of the most active and fascinating topics in nanotechnology. It has been known for several years that the addition of a second metal into monometallic nanoparticles significantly changes some of their properties, e.g. optical properties, catalytic properties, electronic properties, etc. [3-7]. When two or more different elements compose one nanoparticle, the differences in atomic radii are going to influence the way the atoms accommodate. However, very little is known about the crystal structure of bimetallic nanoparticles in the size regime from 0.5 to 2nm [5]. For bimetallic nanoparticles composed of a noble metal and a transition metal, recent experimental results indicate that an icosahedral phase structure is preferred over the others [6]. In the present work we are conducting a complete study of the structure, size, shape, optical response and catalytic properties of single, bimetallic and multimetallic nanoparticles. We have made a systematic study of nanoparticles of Au, Ag, Pt, Pd and their alloys, which are the most interesting systems because of their catalytic applications. An aberration-corrected JEOL 2200FS-AC (S)TEM (with a CEOS GmbH corrector on the illumination side) [8] was used for high-angle annular dark-field (HA-ADF) imaging of Au-Pd nanoparticles ranging from pure element end members, through mixtures including Au₁Pd₅ to Au₅Pd₁. Images of the nanoparticles were compared with appropriate density functional theory (DFT) calculations of model particles. Examples are given below. The Au/Pd system was chosen because of its remarkable catalytic properties for many fine chemical fabrications, deep hydrogenation reactions and Co oxidation [4].

Figure 1a shows a HA-ADF image of a nanoparticle of AuPd (1:1 in atomic composition) in which surface roughness is observed; that roughness is consistent with the DFT calculation of a similar particle, shown in Fig. 1b. Both particle and calculations were obtained in conditions of rapid cooling similar to the one that is used in real catalysis. We show that we can predict complex surface structures that are active sites for a number of different reactions. Figure 2a shows nanoparticles in the Au₁Pd₅ system. It is clear that some atomic columns are significantly brighter than adjacent columns. Figure 2b is an intensity trace over the row of atoms as indicated in Fig 2a. A profile over a single (presumed Pd) atom on the carbon film indicated a peak intensity above background of 400 counts. The discrete jumps of this intensity suggest integral numbers of atoms in the respective columns, but the central intensity peak, if all Pd, represents an unreasonable number of Pd atoms extending above the general surface, so it is likely that one or more Au atoms contribute to the intensity of this column. Full STEM image calculations of a model particle structure taking into account Au and Pd concentrations to match the experimental images should clarify the structure [9].

References

- [1] D. Enache et al. *Science*, **311**, 362 (2006)
- [2] R. Pratti and M. Rossi, *J. Catalysis* **176**, 552 (1998)
- [3] A.M. Venezia, V. La Parola, V. Nicoli and G. Deganello, *J. Catalysis* **212**, 56-62 (2002)
- [4] L. Guzzi, et al., *Surface and Interface Analysis*, **34**(1) 72-75 (2002)
- [5] J.L. Rodriguez-Lopez J.L., et al., *Physical Review Letters* **92**(19) 2004
- [6] M. Jose-Yacaman, et al., *J.Vac. Sci. & Tech. B*, **19**(4) 1091-1103 2001
- [7] J.L. Rodriguez-Lopez, J.M. Montejano-Carrizales and M. J. Yacaman, *Appl. Surf. Sci.*, **219**(1-2) 56 (2003)
- [8] D.A. Blom, L.F. Allard, S. Mishina and M.A. O'Keefe, submitted to *Micros. & Microanal.* (2006)
- [9] Work supported by Asst. Sec. Energy Eff'y. and Renewable Energy, Office of FreedomCAR and Vehicle Tech., HTML User Program, ORNL, managed by UT-Battelle for USDOE (contract DE-AC05-00OR22725).

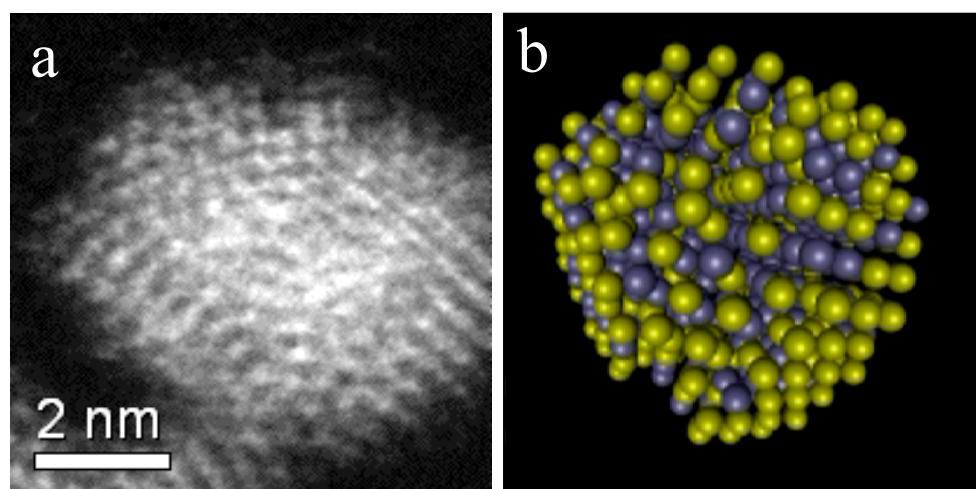


FIG. 1. a) HA-ADF image of particle with nominal Au1Pd1 composition. b) DFT computation of Au1Pd1 nanoparticle, originally created as a perfectly ordered multiply-twinned particle, then heated to 1000K and cooled to RT. The latter, disordered, configuration is a reasonable match to the observed particle, with numerous irregular surface sites.

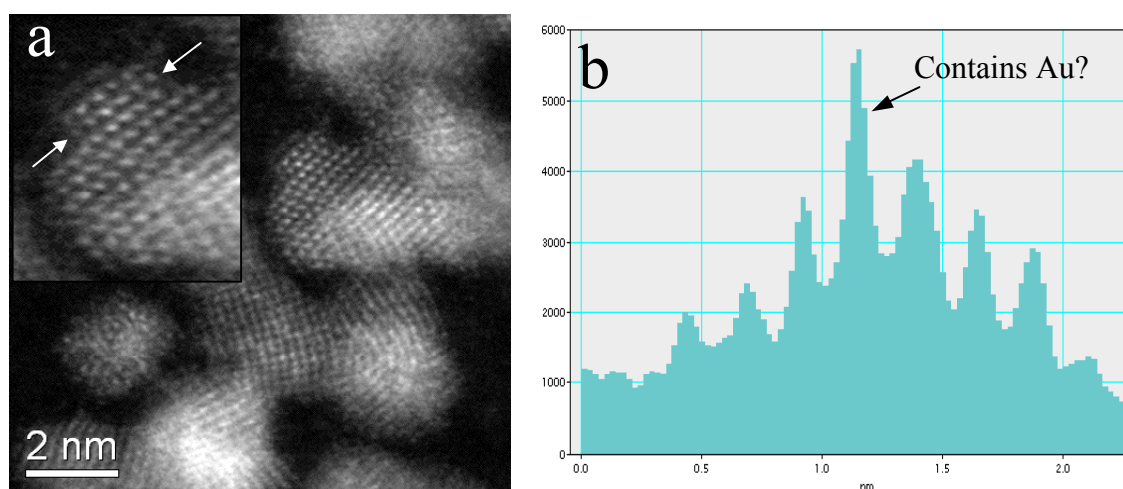


FIG. 2. a) HA-ADF image of Au1Pd5 nanoparticles. b) Profile of intensity of atom row indicated in the inset image of (a). The height of the central atom column suggests one or more Au atoms must be present in the column. Image smoothed using a 3 x 3 low-pass filter.