Giant Pd Clusters Observed by High Resolution Electron Microscopy

Viacheslav V. Volkov,[a,b] Gustaaf Van Tendeloo,[a] Michael N. Vargaftik,[b] Igor P. Stolyarov [b] and Ilya I. Moiseev[b,*]

[a] *EMAT, University of Antwerp, (RUCA), Groenenborgerlaan 171, B-2020 Antwerp, Belgium. Fax: +32 3 218 0257*

[b] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 117907 Moscow, Russian Federation. Fax: +7 095 954 1279*

The giant cationic palladium clusters, approximate formula $Pd_{561}L_{60}(OAc)_{180}$ (L = Dipy, Phen), were characterized by electron diffraction and high resolution microscopy to contain an FCC metal core, most of the larger Pd particles (8 nm) exhibiting multiple twinning, evidence for a distorted icosahedral structure.

Structure analysis of recently synthesized giant cationic palladium clusters,[1,2] has up to now mainly been performed with extensive use of indirect techniques such as EXAFS, SAXS, NMR, IR and magnetic susceptibility measurements. Only occasionally has the real crystal structure of Pd particles been studied by transmission electron microscopy (TEM) and electron diffraction (ED).[1,3–6] Electron diffraction of Pd clusters, with the composition mentioned above, has identified its structure as that of metallic palladium.[6] In this paper we show, using high resolution microscopy, that FCC Pd-clusters with icosahedral elements as well as clusters with a cuboctahedral morphology are present in $Pd_{561}L_{60}(OAc)_{180}$ (L = Dipy, Phen).

The clusters were obtained by the reduction of $Pd(OAc)_2$ with H_2 in acetic acid solutions containing small amounts of Phen or Dipy followed by treatment with O_2 using the method described elsewhere.[2] The material was mildly crushed and glued onto copper grids before investigation in the microscope. TEM experiments were carried out with a 400 kV microscope, with a point resolution of 0.17 nm.

Electron diffraction patterns from both ligated materials revealed no significant difference with respect to the positions of the different rings; a typical example is reproduced in Fig. 1(*a*). The d_{hkl} values of the ring patterns are found to be in agreement with an FCC structure. In the material with L = Dipy one sometimes finds diffraction patterns where the FCC ring pattern clearly consists of discrete reflections; they correspond to areas where the particle size is larger and exceeds 8 nm in size. A low magnification image of an agglomeration of such larger clusters is seen in Fig. 1(*b*); the positions of the diffraction rings, however, does not change. For the samples with L = Phen most of the Pd clusters have a cuboctahedral shape and exhibit a normal distribution of sizes centred at 2.2 nm with a width of 0.4 nm. Fig. 2 shows some of the small clusters and typical features of them. The 2 nm clusters are in general too small to allow much observation of the internal particle structure. Some of the larger clusters, however (in material with L = Dipy), do have a pronounced internal structure (see Fig. 3). Some of them have a cuboctahedral morphology with very little distortion, while other particles show a multiple twinned structure with a local five-fold symmetry (Fig. 3), the so called icosahedron structure. Such five-fold nodes were also observed in larger Pd-particles of icosahedral symmetry prepared by condensation inside an UHV chamber onto *in situ*-grown epitaxial MgO thin films.[4,5] It was shown[4] that the results are in agreement with the 'multiple twinning particle' (MTP) model.

The structure of palladium giant clusters was studied earlier with EXAFS, TEM and electron diffraction techniques.[2,7] The EXAFS data obained for the cluster $Pd_{561}Phen_{60}(OAc)_{180}$ best fitted an icosahedral structure of the metal atoms, whereas the electron microscope study revealed an FCC packing of the Pd atoms. In earlier studies[2] freshly-prepared, well-soluble cluster samples were used. The size distribution was found to be an unimodal one with a maximum at 2.6±0.4 nm. The aged samples, as the ones in this study, also contain larger particles, 8 nm in diameter, which may be formed during lengthy storage.

The EM results show the clusters 2.2 nm in size to exhibit an FCC structure. However, due to the 400 kV electron irradiation, the loss of the ligands, reduction of metal atoms with electron beam and relaxation of the cluster metal core cannot be excluded. The 'naked' metal nuclei of the clusters can be

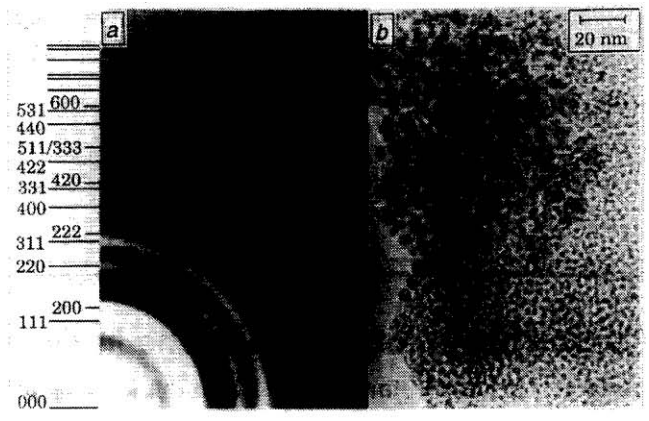

Fig. 1 (*a*) Electron diffraction pattern of $Pd_{561}L_{60}(OAc)_{180}$ (L = Dipy, Phen) showing different rings, identifying the structure as FCC; (*b*) direct image at low magnification of $Pd_{561}L_{60}(OAc)_{180}$ (L = Dipy); note the presence of two different particle sizes.

Fig. 2 High resolution image of the smaller clusters (2.2 nm) in $Pd_{561}L_{60}(OAc)_{180}$ (L = Dipy); very little internal structure is observable.

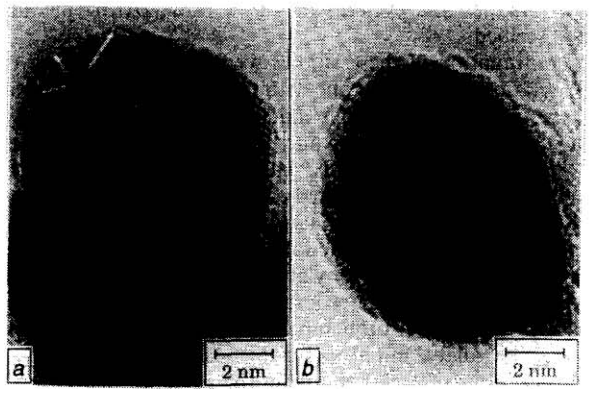

Fig. 3 High resolution image of two of the larger clusters showing multiple twinning.

expected to undergo relaxation to an FCC structure, typical for Pd metal, after eliminating their ligand surrounding.

It is interesting to note in this respect that icosahedral particles were found in the larger particles rather than in small ones. This is possibly caused by faster relaxation of small particles in comparison with that of the larger ones. A slow relaxation to FCC packing was detected earlier by EXAFS data as a result of lengthy storage of the samples under ambient conditions;[8] this process is expected to be accelerated by electron beam heating during TEM experiments.

This paper presents research results of the Belgian programme on Inter University Poles of Attraction initiated by the Belgian State Prime Minister's Office of Science Policy Programming. The scientific responsibility is assumed by the authors. The support by the Russian Fundamental Science Foundation, grant 93–03–4415 for M. N. V., I.P.S. and I. I. M. is also acknowledged.

References

1 M. N. Vargaftik, V. P. Zagorodnikov, I. P. Stolyarov, I. I. Moiseev, V. A. Likholobov, D. I. Kochubey, A. L. Chuvilin, V. I. Zaikovsky, K. I. Zamaraev and G. I. Timofeeva, *J. Chem. Soc., Chem. Commun.*, 1985, 937.
2 M. N. Vargaftik, V. P. Zagorodnikov, I. P. Stolyarov, I. I. Moiseev, D. I. Kochubey, V. A. Likholobov, A. L. Chuvilin and K. I. Zamaraev, *J. Mol. Catal.*, 1989, **53**, 315.
3 S. Giorgio, C. R. Henry and C. Chapon, *J. Crystal Growth*, 1990, **100**, 254.
4 J.-M. Penisson and A. Renou, *J. Crystal Growth*, 1990, **102**, 585.
5 J. Urban, H. Sack-Kongehl, K. Weiss and C. Goyhenen, *Electron Microscopy*, EUREM 92, Granada, Spain, 1992, **2**, 679.
6 M. N. Vargaftik, V. P. Zagorodnikov, I. P. Stolyarov, V. A. Likholobov, A. L. Chuvilin, V. I. Zaikovsky, D. I. Kochubey, G. I. Timofeeva, K. I. Zamaraev and I. I. Moiseev, *Dokl. Akad Nauk SSSR*, 1985, **284**, 896 [*Dokl. Phys. Chem. (Engl. Transl)*, 1985, **284**, 980].
7 G. Schmid, *Chem. Rev.*, 1992, **92**, 1709.
8 D. I. Kochubey, personal communication.

Received: Moscow, 21st May 1993
Cambridge, 21st June 1993: Com. 3/03006G