Determining the energetics of supported bimetallic Au-Pd nanoparticles by aberration-corrected TEM

N. T. Nguyen[1], J. Nelayah[1]*, H. Prunier[1], D. Alloyeau[1], G. Wang[1], L. Piccolo[2], P. Afanasiev[2] and C. Ricolleau[1]

[1] *MPQ, CNRS & Université Paris Diderot, Paris, France*
[2] *IRCELYON, CNRS & Université Lyon 1, Villeurbanne, France*

*jaysen.nelayah@univ-paris-diderot.fr

1. INTRODUCTION

Metallic nanoparticles (NPs) have found applications in a wide variety of fields. While the thermodynamics of NPs is crucial in defining their structure, it can also influence their physical and catalytic properties [1]. Thus, experimental and theoretical studies of the energetics of metallic NPs are very important for promoting existing applications and developing new ones.

In this contribution, we first report on the structural properties of Au-Pd nanoalloys supported on rutile titania. Then, using a recently proposed scheme that combines transmission electron microscopy (TEM) imaging of single nanoparticles and a generalized Wulff-Kaishew theorem [2], the interface and triple-line energies of the Au-Pd NP-titania system are determined experimentally and studied as a function of particle composition and epitaxial relationship.

2. RESULTS

2.1 Experimental conditions

Bimetallic Au-Pd nanoalloys with well-controlled composition were grown on well-defined rutile titania nanorods by pulsed laser deposition. Titania with rod-like shape and narrow size distribution was prepared using a two-step hydrothermal procedure developed by Li and Afanasiev [3]. The nanorods preferentially expose (110) facets. Bimetallic Au-Pd nanoalloys with well-controlled composition were grown on these nanorods by alternate ablation of two monometallic Au and Pd targets in a UHV chamber. During particle nucleation and growth, the rods were kept at a temperature of 300°C, the nominal thickness of deposited metal was 1 nm, and alternate ablation enabled any composition of nanoalloys to be precisely targeted. For ultra-high resolution TEM imaging and X-ray spectroscopy, a JEOL ARM 200F microscope was used. This microscope combines a cold field emission gun and a CEOS hexapole spherical aberration corrector (CEOS GmbH) to compensate for the spherical aberration of the objective lens [4]. The microscope was operated at 80 kV to limit beam damage.

2.2 Structural properties of Au-Pd NPs supported on titania

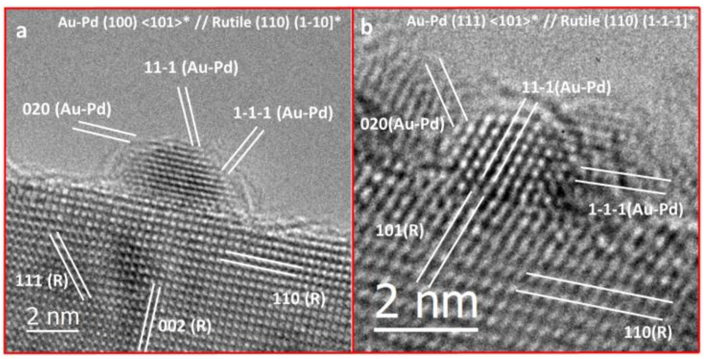

Figure 1. Epitaxially-grown Au-Pd NPs on titania nanorods in (a) Pd(100)<101>*//Rutile(110)[1-10]* and (b) Au-Pd(111)<101>*//Rutile(110)[1-1-1]* epitaxial relationships. The NPs are truncated octahedra bounded by (100) and (111) facets.

Bimetallic nanoparticles with Au, Pd, $Au_{38}Pd_{62}$ and $Au_{57}Pd_{43}$ stoichiometries were synthesized. Their composition was precisely determined by EDX analyses of assemblies of particles. TEM single-particle imaging of the as-synthesized samples showed the formation of well-separated NPs with size range 2-8 nm. As a result of the poor epitaxy between the metallic NPs and their support, most NPs displayed droplet-like morphology with ill-defined crystalline structure. Wherever a higher degree of epitaxy prevailed, Au-Pd NPs in the shape of truncated octahedra and having a completely disordered fcc structure(random alloy) were observed. Various epitaxial relationships were identified between the nanoparticles and the titania support, with the two dominant and previously unreported relationships being Au-Pd(111)<101>*//Rutile(110)[1-1-1]* and Au-Pd(100)<101>*//Rutile(110)[1-10]* (Figure 1).

2.3 Energetics of supported Au-Pd NPs

With the precise equilibrium morphology of the NPs known, the interface and triple-line energies of the metal/oxide systems were determined by combining particle size measurements in atomically-resolved projected TEM images acquired parallel to the metal-oxide interface and a generalized Wulff-Kaishew theorem recently proposed by Sivaramakrishnan *et al.* [4] (Figure 2). This theorem takes into account the influence of triple-line energy on nanoparticle equilibrium shape. Interface and triple-line energies were investigated as a function of particle composition and epitaxy. For any given epitaxial relationship, the relative amplitude of the NP truncation at the interface is found to increase linearly with particle size, *i.e.* the bigger the NP, the more it wets the oxide surface. On the rutile support, analysis of Au, Pd, $Au_{38}Pd_{62}$ and $Au_{57}Pd_{43}$ NPs in epitaxial relationship Au-Pd(111)<101>*//Rutile(110)[1-1-1]* shows clearly that the interface and triple-line energies are strongly influenced by particle composition. The value of the interface energy of the bimetallic Au-Pd NPs $\gamma_{i,Au\text{-}Pd}$ is about 1 J m^{-2}, which is about two and three times that of the monometallic Pd and Au NPs, respectively ($\gamma_{i,Pd} = 0.5 \pm 0.1$ J m^{-2} and $\gamma_{i,Au} = 0.3 \pm 0.2$ J m^{-2}). As for the triple-line energy, it is 0.5 ± 0.1 J m^{-2} for the monometallic nanoparticles. This value is twice the average triple-line energy measured in Au-Pd NPs.

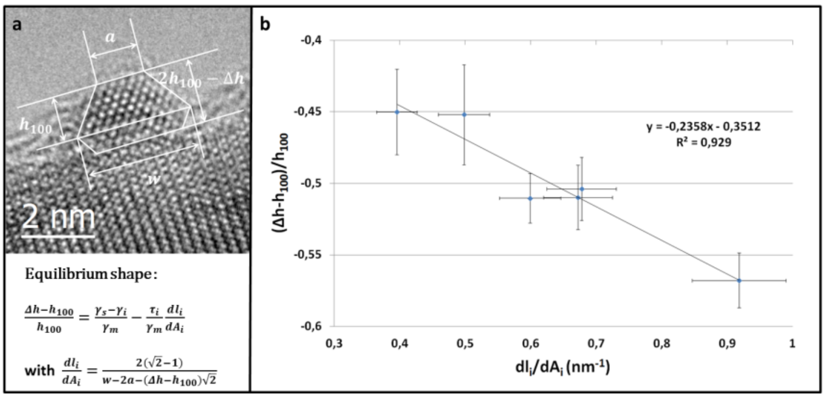

Figure 2. Scheme for the experimental determination of the triple-line and interface energies in epitaxially-supported nanoparticle. (a) High-resolution TEM image of an Au-Pd NP with truncated octahedral equilibrium shape supported on titania. The particle facets and distances of interest for energy determination are indicated. The equation linking the equilibrium particle dimension to the interface energy (γ_i) and triple-line energy (τ_i) of the metal-oxide system is written below the high-resolution TEM image. In this equation, γ_m is the surface energy of the free facet parallel to the support. (b) The values of the triple line and interface energies are extracted from the linear plot of $(\Delta h\text{-}h_{100})/ h_{100}$ against dl_i/dA_i constructed by analyzing different NPs.

3. CONCLUSION

The structural properties of small Au-Pd NPs deposited by laser ablation on titania were studied. Truncated octahedral NPs with fcc structure were identified and their epitaxial relationships with the oxide support determined. With the equilibrium shape of the Au-Pd NPs known and using a modified Wulff-Kaishew theorem, electron microcopy enables the energetics of the metal-oxide systems to be determined as a function of epitaxial relationship and particle composition.

REFERENCES

[1] C. T. Campbell, S. C. Parker and D. E. Starr, *Science* **298**, 811-814 (2004)
[2] S. Sivaramakrishnan *et al*., *Phys. Rev. B* **82**, 195421-195431 (2010)
[3] C H. Li and P. Afanasiev, *Mater. Res. Bull.* ***46***, 2506–2514 (2011)
[4] C. Ricolleau *et al*., *J. Electron Microsc.* **62**, 283-293 (2013)