

## Phase Identification and Diffraction Pattern Indexation for Catalytic Nanostructures

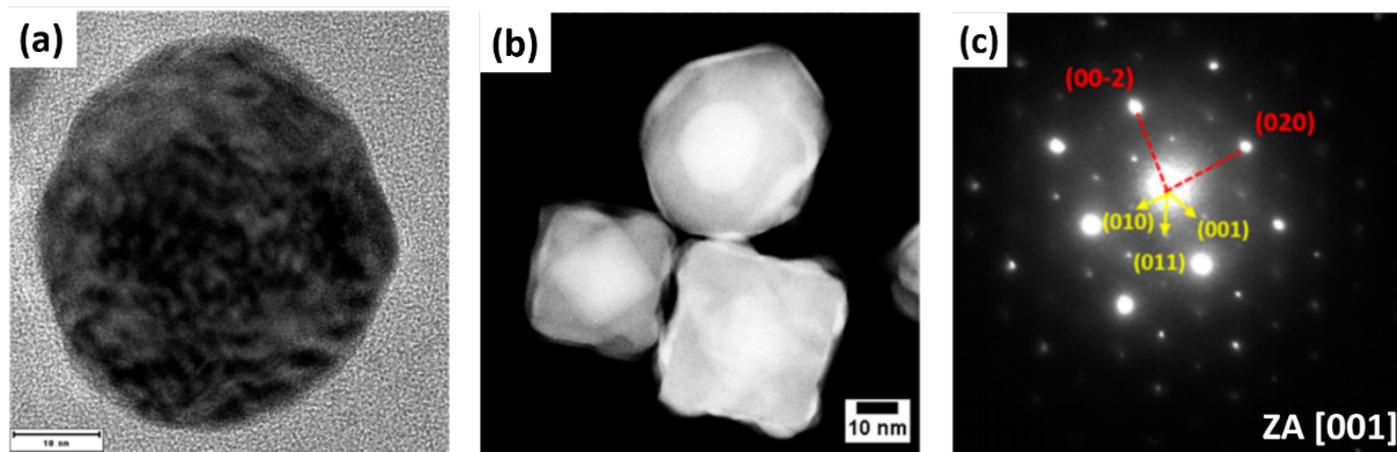
*Electron diffraction analysis of a AuPd model catalyst exhibiting local super-lattice ordering effects triggered by galvanic replacement at the nanoscale level.*

Controlling nanoparticles atomic ordering is of utmost importance in fields such as nanocatalysis, where multiple reactions can occur on the surface of the same nanocatalyst depending on atomic ordering and segregation. These effects are also important in fields such as plasmonics, where the shape, size, composition and degree of chemical ordering determine the energy and intensity of surface plasmon resonances (SPR).

Bimetallic gold-palladium (AuPd) nanostructures are good candidates for nanocatalysis applications since, coupling the two metals not only enhances selectivity towards a much broader range of catalysis reactions, but also increases the tolerance towards poisoning for which Pd is susceptible. The structures presented in this case study are AuPd nanocubes synthesized by the seed-mediated growth method described in Ref. [1]. Figure 1 (a) shows a transmission electron microscopy (TEM) image of

one such nanocube. Typically, these structures contain a Au rich core and a Pd-rich shell, surrounded (or not) by a third, incomplete Au rich layer (see Figure 1 (b)). In the high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image in Figure 1 (b), the Pd rich shell shows a lighter contrast due to the weaker scattering power of the Pd atoms in comparison to that of Au since the observed intensity is proportional to the square of atomic number  $Z$  [2]. The nanobeam diffraction (NBD) pattern displayed in Figure 1 (c) corresponds to the nanocube shown in (a) and displays a cube oriented in  $[001]$  zone axis (ZA).

The pattern contains main reflections (marked with yellow numbers) as well as fainter, secondary reflections, marked with red numbers and arrows, an evidence of chemical ordering, namely a  $L1_2$  superlattice of  $Pd_3Au$  type.



**Figure 1**

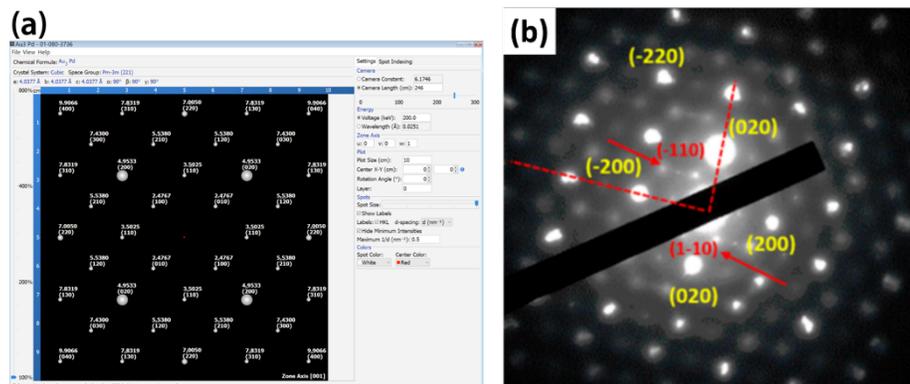
*Transmission electron microscopy (TEM) image of a AuPd nanocube; (b) HAADF-STEM image of a section of two- and three layer AuPd nanocube displaying contrast variations across the atomic columns, resulted following the synthesis method adopted herein; (c) NBD pattern of the AuPd nanocube shown in (a) displaying main and secondary diffraction spots, an indication of superlattice formation of the surface of the nanocubes (see Ref. [1]).*

To index the NBD pattern, an elemental search in the PDF-4+ database has been performed, created by filtering just on Au and Pd elements. The search resulted in a list of compounds containing crystal structure details (e.g. partial atomic coordinates, lattice parameters, space group, etc). The  $Pd_3Au$  compound has been selected (entry 01-080-3739), with a space group  $Pm-3m$  (SG 221) and lattice constants  $a=b=c=3.97 \text{ \AA}$ ,  $\alpha=\beta=\gamma=90^\circ$ . The selected area electron diffraction (SAED) capabilities of PDF-4+ database have been then selected. Fig 2(a). Diffraction pattern simulations are performed based on algorithms developed by R. P. Goehner and J. R. Michael (Ref. [3]). Parameters such as camera length and acceleration voltage

have been adjusted according to the experimental conditions. The simulated diffraction pattern zone axis has been set to  $[001]$ , following *a-priori* information regarding the crystal structure of the compound and from the experimental evaluation of angles between main crystallographic directions. In the PDF-4+ database, the lattice spacings and main angle between crystallographic directions have been measured in the reciprocal space, and compared against the experimental data. Fig.2(b)

The one-to-one comparison confirmed the structure is a superlattice compound, where short range ordering of the minority

species (Au in this case) and majority species (Pd) takes place in the secondary layer of the nanocubes and has been triggered by a galvanic replacement process (see Ref [1]). Such structures can have important applications in model and catalysis reactions, where a controlled ordering process at the nanoscale level is desired for an enhanced selectivity towards various chemical compounds.



**Figure 2 (a).** Snapshot of the SAED capabilities of PDF-4+ software. A snapshot of a simulated electron diffraction pattern of a Pd<sub>3</sub>Au compound is seen here in  $\zeta A [001]$ . The simulation parameters (acceleration voltage, camera length, etc.) have been established following the experimental conditions. The pattern shows main crystal reflections (large diffraction spots) as well as superlattice reflections (smaller, secondary spots), in the forbidden position. The pattern is indicating an ordering of one of the elements (in this case Au) with respect to the parent cell (Pd); (b) an indexed diffraction pattern of the nanocube shown in Figure 1 (a), shown side by side the simulated pattern.

## References

- [1] Calderon, A. L., Bruma, A., Bahena-Urbe, D., Ponce, A., Jose-Yacamán, M., *J. Phys. Chem. C.*, 119, 24621, **2015**.
- [2] Pennycook, S. J., Nellist, P. D. (eds), *Scanning Transmission Electron Microscopy: Imaging and Analysis*, Springer, New York, **2011**.
- [3] Goehner, R. P, Michal, J. R., *Journal of research of the National Institute of Standards and Technology*, 101,301, **1996**.