Shape-Selection of Thermodynamically Stabilized Colloidal Pd and Pt Nanoparticles Controlled via Support Effects

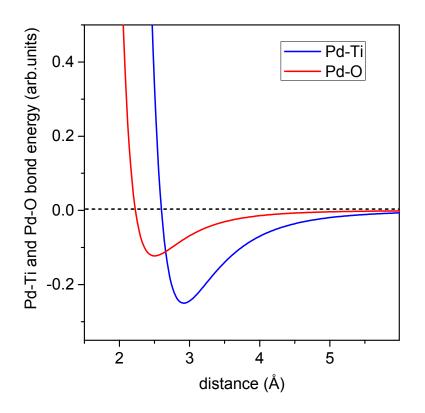M. Ahmadi[1], F. Behafarid[1], C. Holse[2], J. H. Nielsen[2], B. Roldan Cuenya[3*]

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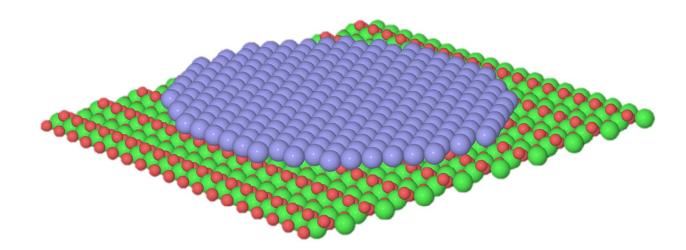
Epitaxial relationship calculations:

To study the mismatch effect in cases of dissimilar lattices, 2D models of the NP interfacial facet and the $TiO_2(110)$ support were constructed using a self-written MATLAB code. By distorting the metal lattice in all possible ways, the best configuration to accommodate the support lattice could be determined. The overall NP-support binding energy is defined based on the energy of Pt-Ti or Pd-Ti bonds following the Lennard-Jones atomic interaction, Suppl. Fig. S1.
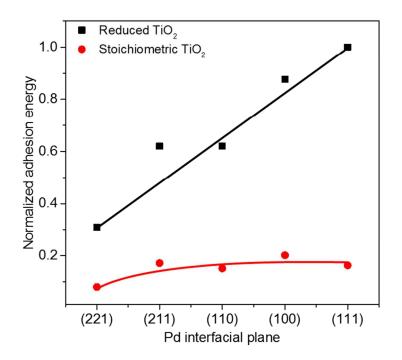
Suppl. Fig. S1: The Leonard Jones potential for Pd-Ti and Pd-O bonds with bond lengths of ~2.6 Å and ~2.1, respectively are shown here.[1]

The interaction energies of each metal atom at the NP interfacial plane and all nearby Ti atoms on the support were added to calculate the overall NP-support adhesion energy. Different Pd and Pt surface orientations were considered, including, (221), (110), (100), (211) and (111). The interfacial metal surface was modified by changing its in-plane rotation angle (θ), the expansion/compression of the Pd (or Pt) lattice in the $TiO_2[001]$ and $TiO_2[1\bar{1}0]$ directions (ε_x, ε_y, respectively), a Pd lattice shift in x and y directions, as well as the gap between the Pd and TiO_2 surfaces (h). The coefficients ε_x or ε_y are defined as $\varepsilon_{x,y}=100\times |L_{bulk}-L_{relaxed}|/L_{bulk}$, where L is the lattice parameter of the Pd (or Pt) surface in the x or y direction. It was found that the optimum strain coefficient ε_x is ~6.8 % for Pt and ~7.6 % for Pd. Such coefficients allow the Pt-Pt and Pd-Pd bond lengths to accommodate the TiO_2 lattice of 2.95Å.

A similar calculation to the one included in the main manuscript (Fig. 6) was conducted on a stoichiometric TiO_2 (110)-(1x1) surface which included bridge oxygen atoms. In this case the contribution to the interfacial adhesion energy was obtained from the interaction between Pd and Pt atoms and bridging oxygen atoms (suppl Fig S2). Following this model, a significantly lower adhesion energy was obtained as a result of the lower bond energy of Pd atoms to oxygen atoms as compared to Ti, as well as to sterically hindered Pd-Ti bonding limiting the adhesion energy to Pd-O_{bridge} bonds[1]

Suppl. Fig. S2: Schematic of the (111) Pd interfacial facet on the TiO_2(1×1) substrate, including bridge oxygen atoms.

Suppl. Fig. S3: Normalized $Pd/TiO_2(110)$ adhesion energy for different Pd interfacial planes plotted for (1x1) TiO_2 surfaces, one stoichiometric, and the other reduced by removing bridge oxygen atoms.

References

(1)   Wanbayor, R.; Ruangpornvisuti, V. A Periodic DFT Study on Binding of Pd, Pt and Au on the Anatase TiO_2 (001) Surface and Adsorption of CO on the TiO_2 Surface-supported Pd, Pt and Au. *Appl. Surf. Science.* **2012**, *258*, 3298-3301.