ESI for thermodynamics of faceted palladium(-gold) nanoparticles supported on rutile titania nanorods studied using transmission electron microscopy†

Nhat Tai Nguyen,[a] Jaysen Nelayah,*[a] Damien Alloyeau,[a] Guillaume Wang,[a] Laurent Piccolo,[b] Pavel Afanasiev,[b] and Christian Ricolleau[a]

1 Notation used to describe the epitaxy of Pd(-Au) NPs on r-TiO_2

The epitaxial relationship between a Pd(-Au) NP and the r-TiO_2 is written as follows: Pd(-Au)(hkl)<uvw> ∥ r-TiO_2(h'k'l')[u'v'w'] where (hkl) and (h'k'l') are respectively the Miller indices of the planes of the NP and of the support in contact. [uvw] and [u'v'w'] are two crystallographic directions of the particle and r-TiO_2 respectively that are parallel to each other and are parallel to the NP-support interface.

2 Dewetting of bimetallic Pd(-Au) NPs on rutile titania

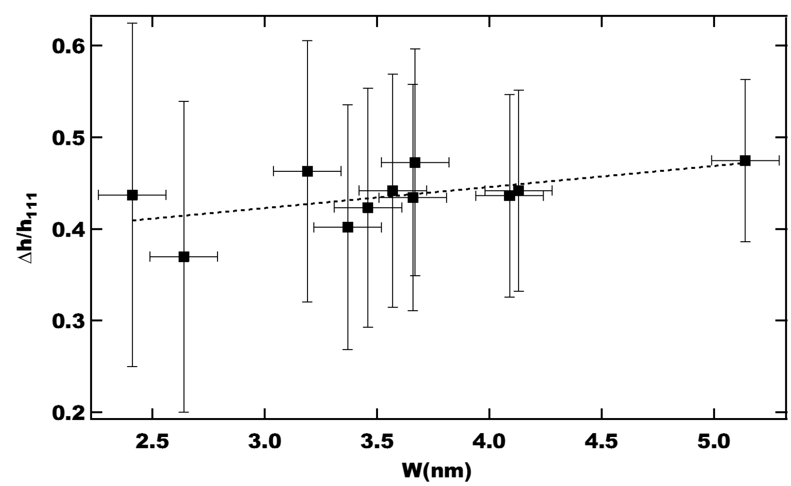

Fig. 1S Dewetting of $Pd_{43}Au_{57}$ NPs in epitaxial relationship $Pd_{43}Au_{57}$(111)<101> ∥ r-TiO_2(110)[1-1-1] as a function of particle size.

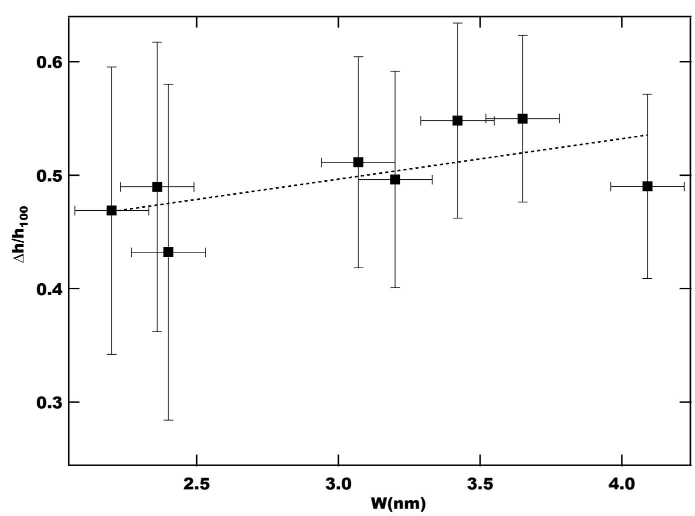

Fig. 2S Dewetting of $Pd_{62}Au_{38}$ NPs in epitaxial relationship $Pd_{62}Au_{38}$(100)<101> ∥ r-TiO_2(110)[1-10] as a function of particle size.

3 Derivation of an extended Wulff-Kaishev rule

A first extension of the Wulff-Kaishev model that takes into account the effect of epitaxial stress on thermodynamic equilibrium shape (ES) of a crystal deposited on a supoport with lattice mismatch was given by P. Müller and R. Kern[1]. In particular, they showed that the expression of the elastic energy stored in a partially relaxed particle of volume V is expressed as $\lambda E\varepsilon^2 V$ where $E\varepsilon^2 V$ is the elastic energy stored in the particle before relaxation. λ is a stress relaxation factor which depends, in complex ways, on the shape of the particle, its orientation with respect to the support and the rigidity of the particle and the support[2]. It varies between 0 and 1. It is 0 for a completely relaxed particle and is 1 in the absence of elastic relaxation. E is a combination of elastic coefficients of the particle and its support and ε is the lattice parameter mismatch between the two systems. According to the theory of nucleation, ΔG, the work necessary to form a polyhedral particle of volume V from its gaseous phase on a planar support with lattice mismatch is the difference between the free energy of the system in its final and initial states plus energy terms related to epitaxial strain and particle surfaces, particle edges and particle-support interface among others[3,4] :

$$\Delta G = -n\Delta\mu + \sum_{j\neq i} \gamma_m^j A_j + (\gamma_i - \gamma_s)A_i + \lambda E\varepsilon^2 V + \sum_k \rho_k l_k + \sum_i \tau_i l_i \tag{S1}$$

where $\Delta\mu$ is the supersaturation per atom. It is the difference in chemical potential between a free atom in gaseous phase (μ_0) and an atom in the particle (μ_p), i.e., $\Delta\mu = \mu_0$ - μ_p. n is the number of atoms in the particle. γ_m^j is the surface energy of free facet j of surface area A_j, γ_s is the surface energy of the support and γ_i is excess energy associated with the formation of the metal-support interface of surface area A_i and of perimeter L_i. τ_i is the excess energy due the particle edge i of length l_i at the particle-support-vacuum triple phase line (or, as in the main text, simply called the triple line) with $\sum_i l_i = L_i$. In comparison, ρ_k is the excess energy due to free edge k of length l_k.

If v is the atomic volume, $V = n.v$. By setting $k = \lambda.v$, equation (S1) can be rewritten as follows:

$$\begin{aligned}
\Delta G &= -\frac{V}{v}\Delta\mu + \sum_{j\neq i} \gamma_m^j A_j + (\gamma_i - \gamma_s)A_i + \lambda E\varepsilon^2 V + \sum_k \rho_k l_k + \sum_i \tau_i l_i \\
&= \left(\lambda E\varepsilon^2 - \frac{\Delta\mu}{v}\right).V + \sum_{j\neq i} \gamma_m^j A_j + (\gamma_i - \gamma_s)A_i + \sum_k \rho_k l_k + \sum_i \tau_i l_i \\
&= \left(\frac{kE\varepsilon^2 - \Delta\mu}{v}\right).V + \sum_{j\neq i} \gamma_m^j A_j + (\gamma_i - \gamma_s)A_i + \sum_k \rho_k l_k + \sum_i \tau_i l_i
\end{aligned}$$

In the main text, we have shown that Pd(-Au) NPs studied here were inhomogeneously strained with no clear dependence between lattice strain and size for any given composition. In the following, the relaxation factor λ will thus be considered as size-independent. We will also neglect the contribution of the particle free edge energies. Indeed, as also discussed in the main text, the free edges in Pd(-Au) NPs marginally influence their ES. Finally, the excess energy along the triple line will be considered isotropic with an average value of τ. Neglecting the anisotropy of the triple line energy leads to $\sum_i \tau_i dl_i = \sum_i \tau dl_i = \tau L_i$. Under these assumptions and neglecting the size dependence of surface and interface energies, the elementary work associated with the nucleation of the particle, d$\Delta G(n)$ is given by:

$$d\Delta G = \left(\frac{kE\varepsilon^2 - \Delta\mu}{v}\right).dV + \sum_{j\neq i} \gamma_m^j dA_j + (\gamma_i - \gamma_s)dA_i + \sum_k \rho_k dl_k + \tau L_i \tag{S2}$$

For a supported particle with polyhedral morphology, its volume V can be divided into congruent pyramids of height h_p and polygonal base area A_p such that :

$$V = \frac{1}{3}\sum_p h_p A_p = \frac{1}{3}\left(\sum_{j\neq i} h_j A_j + (h - \Delta h)A_i\right) \tag{S3}$$

where (h - Δh) is the distance from the centre of the particle to the facet of the particle in contact with the support (Δh being the particle truncation due to the support). h_j is the distance of free facet j (of surface area A_j) from the particle centre. The derivative of V is :

$$dV = \frac{1}{2}\left(\sum_{j\neq i} h_j dA_j + (h - \Delta h)dA_i\right) \tag{S4}$$

Replacing dV in equation (S2) by its expression in equation (S4), we obtain :

$$d\Delta G = \left(\frac{kE\varepsilon^2 - \Delta\mu}{v}\right).\left(\frac{1}{2}(\sum_{j\neq i} h_j dA_j + (h - \Delta h)dA_i)\right) + \sum_{j\neq i} \gamma_m^j dA_j + (\gamma_i - \gamma_s)dA_i + \sum_k \rho_k dl_k + \tau L_i \tag{S5}$$

When the particle reaches its thermodynamic equilibrium shape, all partial derivatives of ΔG cancel out simultaneously. Thus, at equilibrium, any free facet j verifies the following equation:

$$\left(\frac{\partial\Delta G}{\partial A_j}\right)_{\Delta\mu, A_i} = 0 \tag{S6}$$

while at the interface with the support, we have :

$$\left(\frac{\partial\Delta G}{\partial A_i}\right)_{\Delta\mu, A_j} = 0 \tag{S7}$$

From equations (S6) and (S7), we get:

$$\frac{\gamma_i - \gamma_s + \tau \frac{dL_i}{dA_i}}{h - \Delta h} = \frac{\Delta\mu - kE\varepsilon^2}{3\nu} \tag{S8}$$

and

$$\frac{\gamma_m}{h} = \frac{\Delta\mu - kE\varepsilon^2}{3\nu} \tag{S9}$$

respectively.

By combining equations (S8) and (S9), we obtain the extented Wulff-Kaishev rule incorporating the effect of the triple line energy on the thermodynamic ES of the particle:

$$\frac{\Delta h - h}{h} = \frac{\gamma_s - \gamma_i}{\gamma_m} - \frac{\tau}{\gamma_m}\frac{dL_i}{dA_i} \tag{S10}$$

$\frac{dL_i}{dA_i}$ is a geometric factor which varies form one particle to another depending on the geometry of the particle-support interface. The latter is defined by the morphology of the particle and its orientation relatively to the support. In this work, this factor is expressed simply in terms of measurable distances on high resolution transmission electron microscopy (HRTEM) images of single NPs acquired parallel to the particle-support interface as shown in the following and in the main text. In the following sections, we will establish $\frac{dL_i}{dA_i}$ for a supported face-centered cubic (FCC) particles with octahedral truncated ES in two distinct orientations with respect to the support.

4 Expression of the geometric factor $\frac{dL_i}{dA_i}$

4.1 Truncated octahedral FCC particle supported on its (010) facet

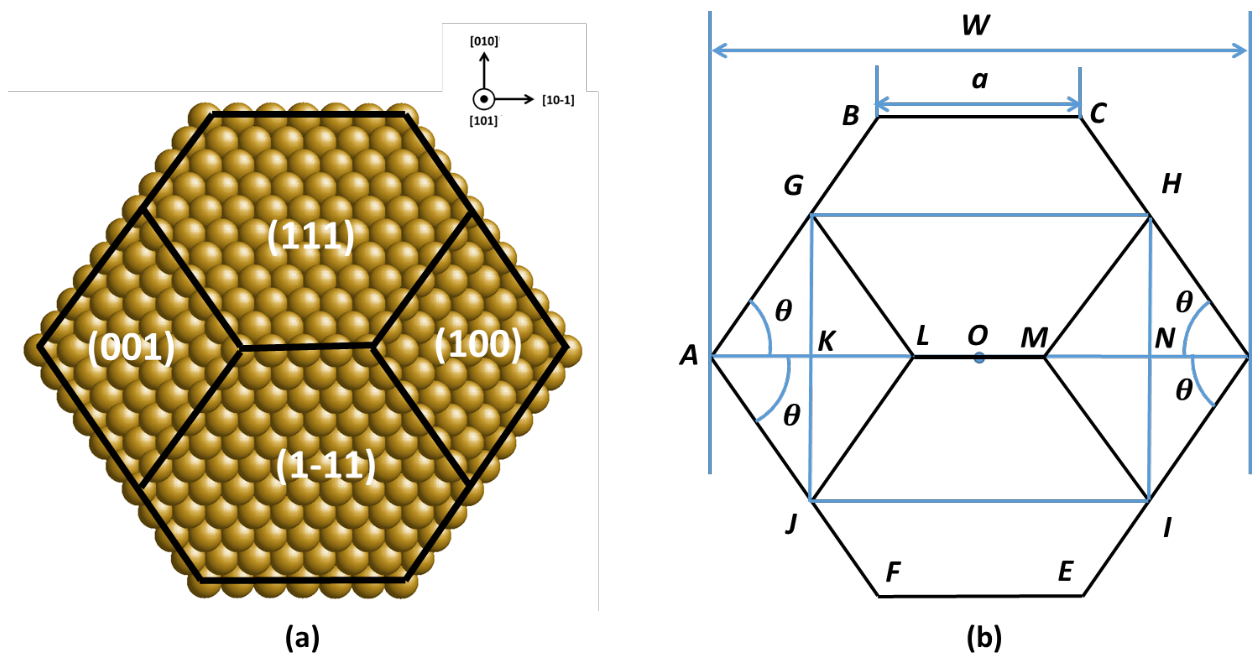

Fig. 3S (a) Atomic model of a free FCC particle with truncated octahedral morphology along the [101] zone axis. Visible facets and their indices are indicated; (b) Outline of the projection of the particle in [101] zone axis. Square (100) facets of sides length a can be distinguished. O is the centre of the projection and W is the width of the particle in zone axis.

Fig. 3Sa shows an atomic model of a free truncated octahedral particle with closed-packed FCC structure in [101] zone axis. The particle is limited by (100) and (111) facets. The (100) facets have a square shape of side length a. Let W denotes the width of the particle in this projection, i.e. its lateral extension along the [10-1] direction (Fig. 3Sb).

From the outline of the particle projection along the [101] direction, we show that :

- GJ being the diagonal of a (100) facet, $GJ = HI = a\sqrt{2}$.
- Isolating parallelogram $ABCLA$, $AL = BC = a$. By symmetry, $MD = a$. Thus, $JI = W$ - a and $LM = W$ - $2a$.

- $\widehat{ABC} = \widehat{ADE} = \widehat{DAB} = \widehat{DAF} = \theta$ with θ being the angle between the (100) and (111) planes. We can thus write $\cos\theta = \frac{(111).(100)}{|111||100|} = \frac{1}{\sqrt{3}}$ and deduce that $\tan\theta = \sqrt{2}$.

When the particle is deposited on a support, the particle will present an extra truncation at the particle-support interface. Fig. 4Sa shows the outline of the projection of a supported truncated octahedral particle with one of its (100) facet in contact with the support. The particle is truncated at its base by a length Δh. Let's first consider the length of segment PQ. From Fig. 4Sa, the length of segment PQ is expressed as :

- $PQ = OP$ - $OQ = OP$ - $KJ = h_{100}$ - $\frac{a}{\sqrt{2}}$.

Two types of truncation are possible depending on the difference between the length of segment PQ and particle truncation Δh. If $\Delta h >$ PQ, the interface will have an octagonal shape (Fig. 4Sb). Otherwise, the interface will be a square (Fig. 5Sb). We will now determine the expression of $\frac{dL_i}{dA_i}$ in each case.

4.1.1 $\Delta h > PQ$

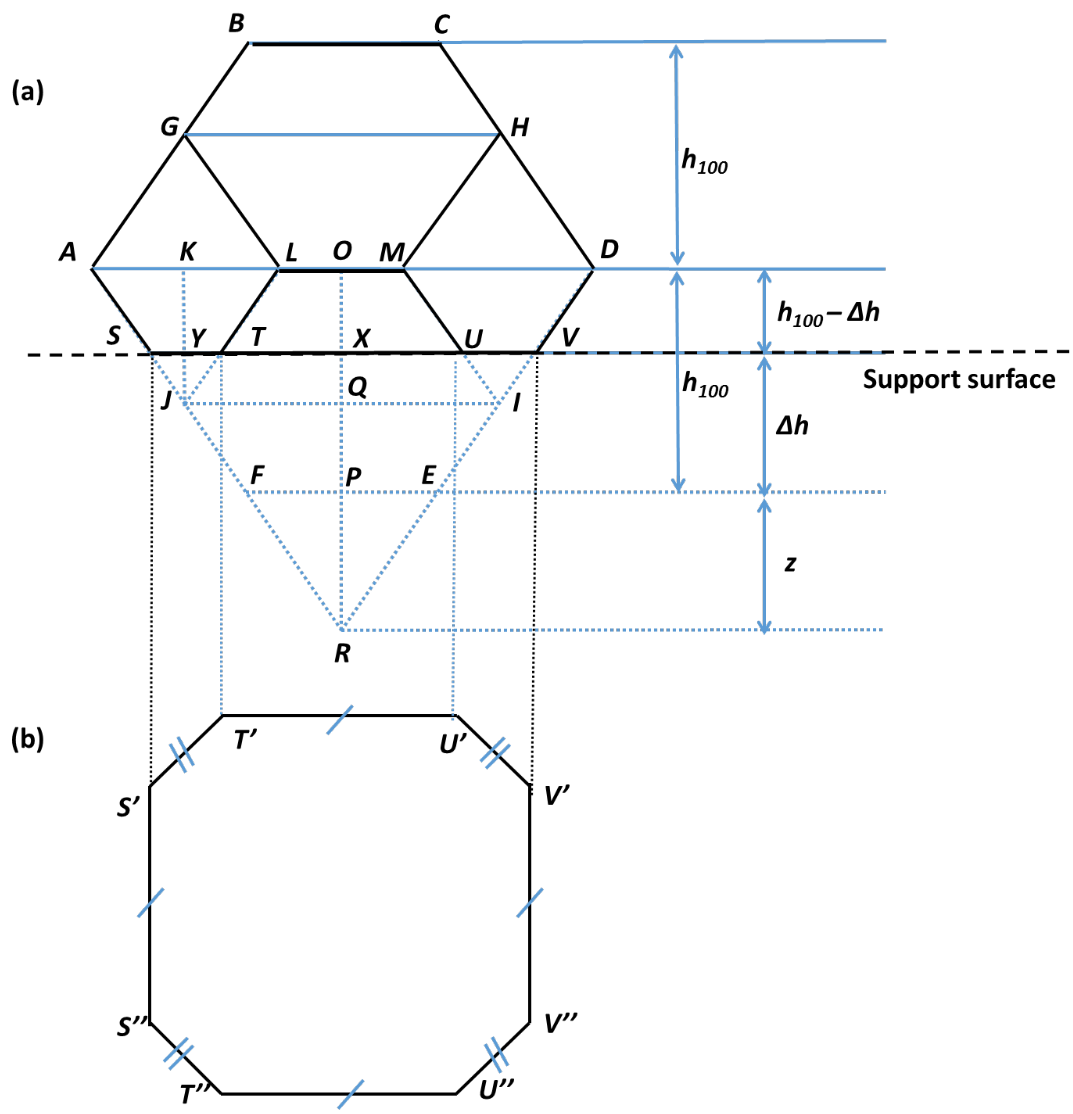

Fig. 4S(a) Outline of the projection of a supported truncated octahedral FCC particle in [101] zone axis deposited on a (100) facet (black lines). Construction lines are shown in light blue. Point R is at the intersection of the half-lines AF and DE. P and Q are the intersections between the segment RO and segment JI and FE, respectively. We set $z = PR$ and $h_{100} = OP$. (b) Outline of the particle-support interface for Δh $> PQ$. The interface is here of octagonal shape defined by segments $S'T'$ and $T'U'$.

By geometrical construction on Fig. 4Sa:

$$\begin{aligned} SV &= \frac{RX}{RO}.AD \\ &= \frac{z+\Delta h}{z+h_{100}}.AD \\ &= (1+\frac{\Delta h - h_{100}}{z+h_{100}}).AD \end{aligned}$$

Since,

- $OR = AO.\tan\theta = \frac{W}{2}\sqrt{2}$

and $OR = z + h_{100}$, we deduce :

$$z + h_{100} = \frac{W}{\sqrt{2}} \quad \text{(S11)}$$

Consequently, SV can be simplified as follows :

$$\begin{aligned} SV &= (1+\frac{\Delta h - h_{100}}{\frac{W}{\sqrt{2}}}).W \\ &= W + (\Delta h - h_{100})\sqrt{2} \end{aligned}$$

Moreover,

$$\begin{aligned} ST &= UV \\ &= \frac{QX}{QO}.AL \\ &= \frac{\Delta h - PQ}{QX+XO}.AL \\ &= \frac{\Delta h - h_{100} + \frac{a}{\sqrt{2}}}{\frac{a}{\sqrt{2}}}.a \\ &= a + (\Delta h - h_{100})\sqrt{2} \end{aligned}$$

From these two distances, we can express the length of segments $S'T'$ and $T'U'$ which define the octagonal interface (Fig. 4Sb) as follows:

$$\begin{aligned} S'T' &= S''T'' = U'V' = U''V'' \\ &= ST\sqrt{2} \\ &= a\sqrt{2} + 2(\Delta h - h_{100}) \end{aligned}$$

and

$$\begin{aligned} T'U' &= SV - ST - UV \\ &= W + (\Delta h - h_{100})\sqrt{2}) - 2(a + (\Delta h - h_{100})\sqrt{2}) \\ &= W - 2a - (\Delta h - h_{100})\sqrt{2} \end{aligned}$$

Using Fig. 4Sb and by setting $T'U' = a_i$, the expressions for the perimeter L_i and the surface area A_i of the octagonal particle-support interface are as follows:

$$\begin{aligned} L_i &= 4(S'T' + T'U') \\ &= 4(a\sqrt{2} + 2(\Delta h - h_{100}) + a_i) \\ &= 4(a\sqrt{2} + 2\frac{W-2a-a_i}{\sqrt{2}} + a_i \\ &= 4(1-\sqrt{2})a_i + 4\sqrt{2}(W-a) \end{aligned}$$

$$\begin{aligned} A_i &= SV^2 - S'T'^2 \\ &= (W + (\Delta h - h_{100})\sqrt{2})^2 - (a\sqrt{2} + 2(\Delta h - h_{100}))^2 \\ &= (W + \frac{W-2a-a_i}{\sqrt{2}}\sqrt{2})^2 - (a\sqrt{2} + 2\frac{W-2a-a_i}{\sqrt{2}})^2 \\ &= (2W - 2a - a_i)^2 - ((W-a)\sqrt{2} - a_i\sqrt{2})^2 \\ &= 2(W-a)^2 - a_i^2 \end{aligned}$$

Deriving the expressions of L_i and A_i with respect to a_i (and considering the variations of L_i and A_i with a to be marginal), we get

âĂć dL_i = 4(1 - $\sqrt{2}$)da_i

âĂć dA_i = -2a_ida_i

from which we deduced the expression of the geometric factor $\frac{dL_i}{dA_i}$ for $\Delta h > PQ$:

$$\frac{dL_i}{dA_i} = \frac{2(\sqrt{2}-1)}{a_i} = \frac{2(\sqrt{2}-1)}{W-2a-(\Delta h-h_{100})\sqrt{2}} \tag{S12}$$

The geometric factor can be easily calculated with W, a, h_{100} and Δh known. All these dimensions are directly measurable on a HRTEM image of the particle in [101] zone axis.

4.1.2 Δh ≤ PQ

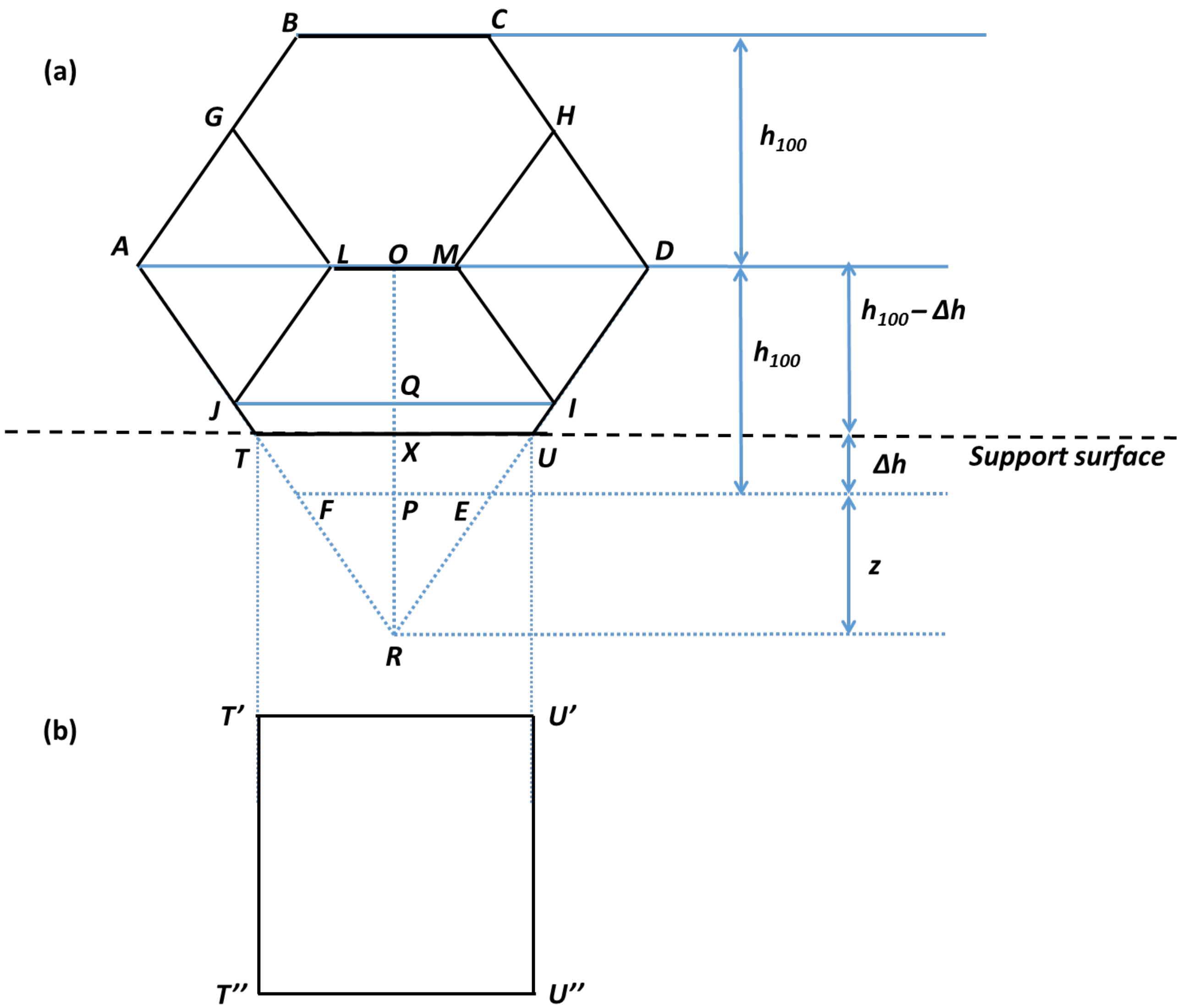

Fig. 5S (a) Outline of the projection of a supported truncated octahedral FCC particle in [101] zone axis deposited on a (100) facet when Δh ≤ PQ (b) Outline of the square particle-support interface defined by segment $T'U'$. Particle-support when Δh < PQ for a truncated octahedral particle with one of its (100) facets in contact with the support. The interface has here a square shape.

When the shape of the particle-support interface is a square of side length b_i (Fig. 5Sb),

$$\begin{aligned} T'U' &= b_i \\ &= \frac{RX}{RO}.AD \\ &= \frac{z+\Delta h}{z+h_{100}}.W \\ &= \frac{z+h_{100}+\Delta h-h_{100}}{z+h_{100}}.W \\ &= (1+\frac{\Delta h-h_{100}}{z+h_{100}}).W \end{aligned}$$

Moreover, as according to equation (S11), $z + h_{100} = \frac{W}{\sqrt{2}}$, b_i simplifies to:

$$b_i = W + (\Delta h - h_{100})\sqrt{2}$$

Since the interface is a square, $L_i = 4b_i$ and $A_i = b_i^2$. By calculating the derivatives dL_i and dA_i with respect to b_i, we obtain :

$$\frac{dL_i}{dA_i} = \frac{2}{b_i} = \frac{2}{W + (\Delta h - h_{100})\sqrt{2}} \tag{S13}$$

In this configuration, the determination of $\frac{dL_i}{dA_i}$ only requires the knowledge of the W, Δh and h_{100}.

In our study of $Pd_{62}Au_{38}$ NPs in epitaxial relationship $Pd_{62}Au_{38}(100)$<101> ∥ r-$TiO_2(110)$[1-10], all NPs displayed ES satisfying Δh > PQ. Hence, the expression of $\frac{dL_i}{dA_i}$ given by equation (S12) was used in the main text to describe the morphology of these NPs.

4.2 Truncated octahedral FCC particle supported on its (111) facet

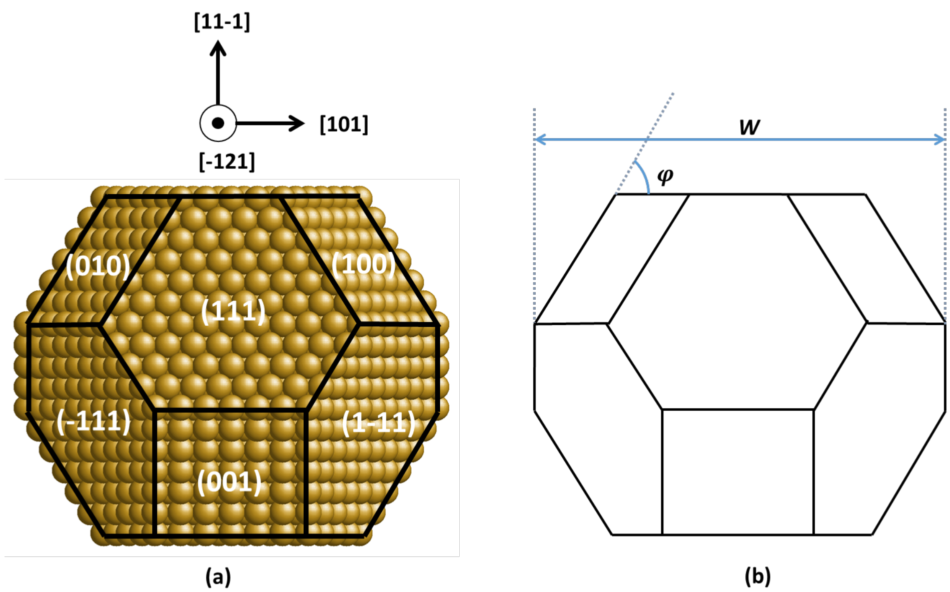

Fig. 6S (a) Atomic model of a free FCC particle with truncated octahedral shape viewed along the [-121] zone axis. Visible facets and their indices are indicated. (b) Outline of the projection of the particle in the same zone axis. W is the width of the particle in this projection. φ is the angle between the (-113) and (11-1) planes.

Fig. 6Sa shows an atomic model of a free FCC particle with truncated octahedral morphology viewed along along [-121] zone axis. If the particle is supported on one of its its (111) facet, the expression of $\frac{dL_i}{dA_i}$ is, according to[5], given by :

$$\frac{dL_i}{dA_i} = \frac{2\sqrt{3}}{W + \frac{2\Delta h}{\tan\varphi}} \tag{S14}$$

where W is the width of the particle along the [10-1] direction with $W = h_{111}\sqrt{6}$, Δh the truncation of the particle at its base and φ the angle between the (-11-3) and (11-1) planes of the FCC lattice leading to $\tan\varphi = 2\sqrt{\frac{2}{3}} = 1.633$ (Fig. 6Sb). In this work, all monometallic Pd and bimetallic $Pd_{43}Au_{57}$ nanodecahedra in epitaxial relationship Pd(-Au)(111)<101> ∥ r-$TiO_2(110)$[1-1-1] were imaged in [101] zone axis. The latter is rotated from [-121] direction by 90 around the [11-1] direction. Although the expression of $\frac{dL_i}{dA_i}$ is independent of zone axis along which a NP is viewed, neither W nor Δh can be straightforwardly determined in [101] zone axis.

To express $\frac{dL_i}{dA_i}$ in terms of measurable distances in [101] zone axis, let's consider Fig. 7S. Fig. 7Sa shows an atomic model of a particle in [101] zone axis. The outline of the projection is shown in Fig. 7Sb.

Since, the expression of $\frac{dL_i}{dA_i}$ in [101] zone axis is the same as in equation (S14), we can write :

$$\begin{aligned}\frac{dL_i}{dA_i} &= \frac{2\sqrt{3}}{W + \frac{2\Delta h}{\tan\varphi}} \\ &= \frac{2\sqrt{3}}{h_{111}\sqrt{6} + \frac{2\Delta h}{2\sqrt{\frac{2}{3}}}}\end{aligned}$$

which simplifies to :

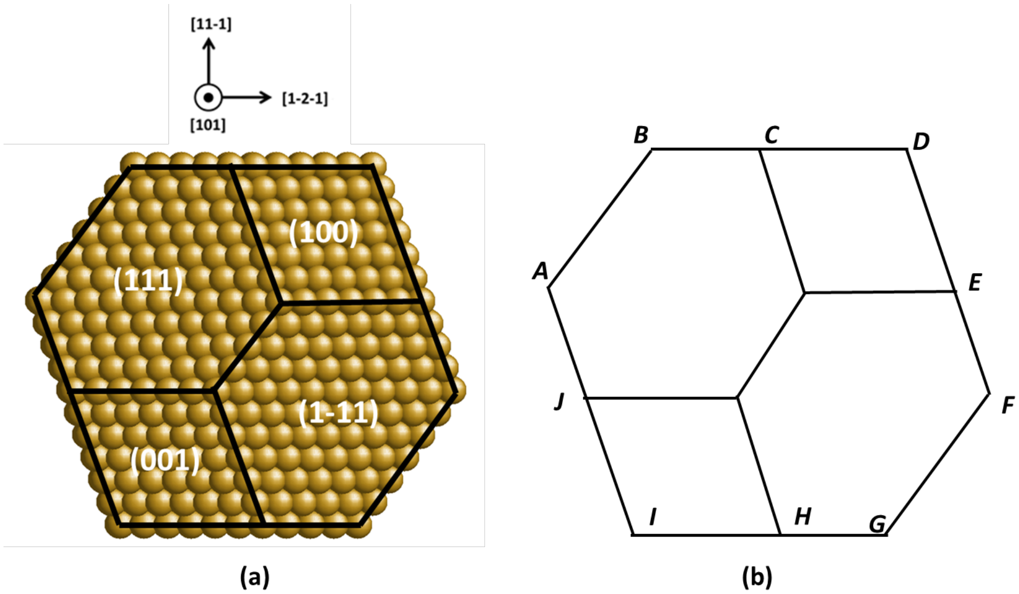

Fig. 7S (a) Atomic model of a free FCC particle with truncated octahedral shape viewed along the [101] zone axis Visible facets and their indices are indicated. (b) Outline of the projection of the particle according to the same zone axis.

$$\frac{dL_i}{dA_i} = \frac{2\sqrt{2}}{\Delta h + 2h_{111}} \tag{S15}$$

The geometric factor $\frac{dL_i}{dA_i}$ is here expressed as a function of Δh and h_{111}. Both distances can be determined from a projected image of a supported FCC truncated octahedron in [101] zone axis as explained in the rest of this section. Fig. 8Sa (top) shows the hexagonal shape of the (111) facet in contact with the support. The point O' corresponds to the perpendicular projection of the particle center O of the NP on this facet. Due to the symmetry of the particle, O' is at the center of the hexagon. However, O' does not lie in the middle of segment $L'N'$ (L' and N' are in the middle of the segments $B'B''$ and $D'D''$ respectively) as the hexagon $B'B''C''D''D'C'B'$ is not regular. It results that the position of particle centre O is also not known. Thus, the value of the truncation Δh and h_{111} are not directly measurable on the two-dimensional projection $ABDFRQPA$ of the particle along [101] zone axis.

To determine Δh and h_{111}, we proceed as follows. The extensions of segments BD and PA meet at point K (Fig. 8Sa). Similarly, the extensions of segments $B'C'$, $B''C''$ and $D'D''$ delimiting the (111) facet form a triangle $K'P'Q'$ (Fig. 8Sb). Note that $K'P'Q'$ is an equilateral triangle of center O'. Hence, for an equilateral triangle, we have $K'O' = \frac{2}{3}K'N'$.

Since $K'N' = KD$, we have $K'O' = \frac{2}{3}KD$. KD can be determined from the projection of the particle in [101] zone axis. Let us now express $K'O'$ in terms of h_{111}. Let's consider OKO'' which is a right-angled triangle with $\widehat{KOO''}$ the angle between the (111) and (100) planes. As $K'O' = KO''$ and $OO'' = h_{111}$, we get $KO'' = OO''.\tan\theta = h_{111}.\sqrt{2}$. Hence,

$$h_{111} = \frac{\sqrt{2}}{3}.KD \tag{S16}$$

Once h_{111} is known, Δh that can be deduced from the measurement of the particle height which is equal to $2h_{111}$ - Δh (Fig. 8Sa).

Notes and references

1 P. Muller and R. Kern, *Surface Science*, 2000, **457**, 229–253.
2 R. Kern and P. Muller, *Surface Science*, 1997, **392**, 103–133.
3 D. Kashchiev, *Nucleation : Basic theory with applications*, Butterworth-Heinemann, 2000.
4 P. Muller and C. Mottet, *Journal of Computational and Theoretical Nanoscience*, 2007, **4**, 316–325.
5 S. Sivaramakrishnan, J. Wen, M. E. Scarpelli, B. J. Pierce and J.-M. Zuo, *Physical Review B*, 2010, **82**, 195421.

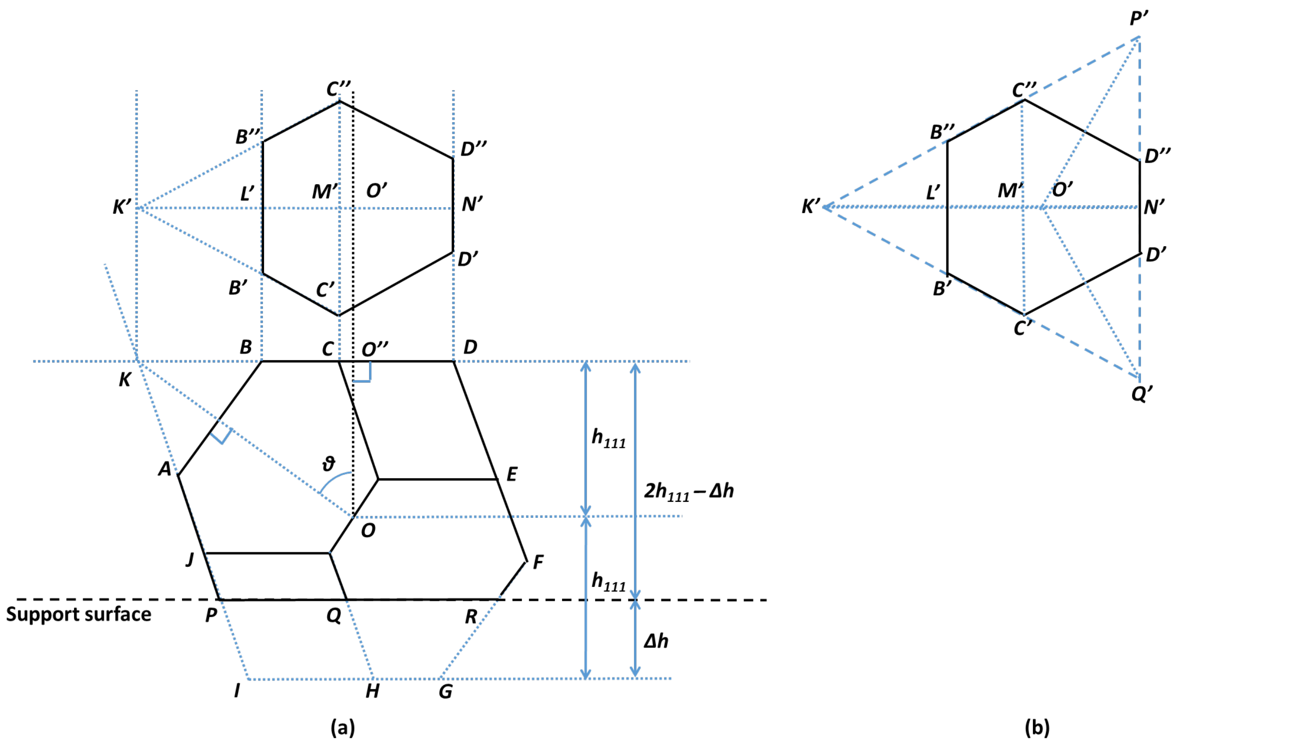

Fig. 8S (a) (top) Projection of the hexagonal facet (11-1) up and (bottom) projection of the cross section of the NP along the [101]; (b) Schematic of the equilateral triangle drawn from this facet by geometrical construction.