Supplementary Information

Shape Control in Concave Metal Nanoparticles by Etching

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S1. Pt surfaces

The surface energy $\gamma_s$, that describes the stability of a surface, is the energy required to cleave a surface from a bulk crystal. It is given by

$$\gamma_s = \frac{1}{2A}(E_s^\text{unrelax} - NE_b) + \frac{1}{A}(E_s^\text{relax} - E_s^\text{unrelax})$$

(1)

Here, $A$ is the area of the surface considered, $E_s^\text{relax}$ and $E_s^\text{unrelax}$ the energies of the relaxed and unrelaxed surfaces, respectively, $N$ the number of atoms in the slab and $E_b$ the bulk energy per atom. For stepped surfaces, we have defined a surface atom as that having less than 12 neighbors. The calculated surface energies are listed in Table S1.

Table S1  Calculated surface energies, $\gamma_s$, at the PBE level and experimental data, $\gamma_{\exp}$.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$\gamma_s$ (Jm$^{-2}$)</th>
<th>$\gamma_{\exp}$ (Jm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(100)</td>
<td>1.87$^a$, 1.81$^b$, 1.84$^c$</td>
<td>-</td>
</tr>
<tr>
<td>Pt(110)</td>
<td>1.93$^a$, 1.85$^b$, 1.68$^c$</td>
<td>-</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>1.67$^a$, 1.49$^b$, 1.48$^c$</td>
<td>2.49$^d$</td>
</tr>
<tr>
<td>Pt(211)</td>
<td>1.70$^a$</td>
<td>-</td>
</tr>
<tr>
<td>Pt(311)</td>
<td>1.81$^a$</td>
<td>-</td>
</tr>
<tr>
<td>Pt(411)</td>
<td>1.80$^a$</td>
<td>-</td>
</tr>
<tr>
<td>Pt(511)</td>
<td>1.81$^a$</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Present study  
$^b$ Reference 1  
$^c$ Reference 2  
$^d$ Reference 3

S2. Adsorption of HCl on Pt surfaces

Adsorption was only allowed on one of the sides of the slab and the configuration with the lowest energy was chosen. The adsorption energies of the HCl molecules were calculated with respect to the solution as follows:

$$BE_{HCl} = (E_{s-HCl} - E_s - E_{HCl}^{solv})$$

(2)

where $E_{s-HCl}$ is the energy of the surface covered with the HCl molecules, $E_s$ is the energy of the clean surface, and $E_{HCl}^{solv}$ is the energy of the solvated HCl. This last quantity was calculated using
VASP-MGCM (VASP-Multigrid Continuum Model), a continuum solvation model developed in our group.\(^4\) In this case, the generalized Poisson equation is solved by means of a multigrid solver, being the local dielectric permittivity \(\varepsilon\) approximated as that of Fattebert and Gygi,\(^5\)

\[
\varepsilon(r) = 1 + \frac{\varepsilon_0 - 1}{1 + (\rho_{el}(r)/\rho_0)^{2\beta}}
\]  

(3)

Here, \(\rho_{el}\) stands for the electronic charge density, \(\varepsilon_0\) is the permittivity of the bulk phase of the solvent (78.5 for water), and \(\rho_0\) and \(\beta\) are parameters controlling the shape of \(\varepsilon\). The adopted values for these two parameters, \(\beta = 1.7\), and \(\rho_0 = 6 \cdot 10^{-4}\) a.u, are the ones that our group has used in all the published studies considering solvation effects.

The adsorption energies of HCl on the Pt surfaces are listed in Table S2. The largest value for the adsorption energy per HCl molecule is that for the Pt(100) surface. For completeness, we also provide the adsorbate-adsorbate and adsorbate-metal shortest distances in Table S3.

**Table S2** Adsorption energies \(BE_{\text{HCl}}\) of HCl on Pt surfaces with the densest coverage. Here, \(\theta\) stands for the HCl coverage, \(n\) is the number of adsorbed HCl molecules, and \(A\) the area of the surface.

<table>
<thead>
<tr>
<th>Surface</th>
<th>(\theta)</th>
<th>(BE_{\text{HCl}}) (eV)</th>
<th>(BE_{\text{HCl}}/n) (eV)</th>
<th>(BE_{\text{HCl}}/A) (eV/Å(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(100)</td>
<td>0.50</td>
<td>-2.22</td>
<td>-1.11</td>
<td>-0.07</td>
</tr>
<tr>
<td>Pt(110)</td>
<td>0.67</td>
<td>-6.49</td>
<td>-0.81</td>
<td>-0.05</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>0.50</td>
<td>-0.96</td>
<td>-0.48</td>
<td>-0.04</td>
</tr>
<tr>
<td>Pt(211)</td>
<td>0.67</td>
<td>-0.12</td>
<td>-0.06</td>
<td>-0.01</td>
</tr>
<tr>
<td>Pt(311)</td>
<td>0.50</td>
<td>-1.11</td>
<td>-0.55</td>
<td>-0.04</td>
</tr>
<tr>
<td>Pt(411)</td>
<td>0.50</td>
<td>-2.88</td>
<td>-0.29</td>
<td>-0.02</td>
</tr>
<tr>
<td>Pt(511)</td>
<td>0.67</td>
<td>-0.40</td>
<td>-0.20</td>
<td>-0.02</td>
</tr>
</tbody>
</table>

**Table S3** Shortest atom-atom distances (in Å) on Pt surfaces at the densest coverage (Cl, H and Pt stand for chloride, hydrogen and platinum surface, respectively).

<table>
<thead>
<tr>
<th>Surface</th>
<th>Cl···Cl</th>
<th>Cl···Pt</th>
<th>Cl···H</th>
<th>H···H</th>
<th>H···Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(100)</td>
<td>3.967</td>
<td>2.396</td>
<td>2.948</td>
<td>3.967</td>
<td>1.719</td>
</tr>
<tr>
<td>Pt(110)</td>
<td>3.652</td>
<td>1.690</td>
<td>2.806</td>
<td>2.405</td>
<td>1.589</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>4.857</td>
<td>2.299</td>
<td>2.894</td>
<td>2.803</td>
<td>1.552</td>
</tr>
<tr>
<td>Pt(211)</td>
<td>2.775</td>
<td>2.351</td>
<td>2.464</td>
<td>2.775</td>
<td>1.707</td>
</tr>
<tr>
<td>Pt(311)</td>
<td>2.805</td>
<td>2.266</td>
<td>3.025</td>
<td>2.805</td>
<td>1.808</td>
</tr>
<tr>
<td>Pt(411)</td>
<td>3.153</td>
<td>2.270</td>
<td>1.831</td>
<td>2.859</td>
<td>1.561</td>
</tr>
<tr>
<td>Pt(511)</td>
<td>2.805</td>
<td>2.331</td>
<td>2.494</td>
<td>2.805</td>
<td>1.727</td>
</tr>
</tbody>
</table>
S3. Wulff construction

The surface energy, $\gamma^0_{HCl}$, for a HCl-covered Pt surface at $T = 0$ K is given by

$$\gamma^0_{HCl} = \gamma_s + \frac{BE_{HCl}}{A}$$  \hspace{1cm} (4)

The equilibrium morphology of the nanoparticles (Fig. S2) was obtained through the Wulff construction method,\textsuperscript{6} which depends on the relative surface energies (Table S4). Therefore, systematic deviations between calculated and experimental surface energies do not affect the reconstructed nanoparticle shape. The crystal morphology model was created with VESTA (Visualization for Electronic and STructural Analysis) version 3.1.8 package.\textsuperscript{7}

![Wulff construction](image)

**Fig. S1** Wulff construction for the naked Pt nanoparticle (left) and HCl-covered Pt system, with the densest coverage (right) using the calculated surface energies of Table S4. Color code: (100) in green, (110) in blue, (111) in dark yellow, (211) in orange, (311) in red, (411) in purple and (511) in wine.

**Table S4** Surface energy for uncovered surfaces, $\gamma_s$, binding energy divided by area $BE_{HCl}/A$, and surface energy for the HCl-covered surfaces with the densest coverage at $T = 0$ K, $\gamma^0_{HCl}$.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$\theta$</th>
<th>$\gamma_s$ (Jm$^{-2}$)</th>
<th>-BE/A (Jm$^{-2}$)</th>
<th>$\gamma^0_{HCl}$ (Jm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(100)</td>
<td>0.50</td>
<td>1.87</td>
<td>1.13</td>
<td>0.74</td>
</tr>
<tr>
<td>Pt(110)</td>
<td>0.67</td>
<td>1.93</td>
<td>0.78</td>
<td>1.15</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>0.50</td>
<td>1.67</td>
<td>0.56</td>
<td>1.10</td>
</tr>
<tr>
<td>Pt(211)</td>
<td>0.67</td>
<td>1.70</td>
<td>0.10</td>
<td>1.61</td>
</tr>
<tr>
<td>Pt(311)</td>
<td>0.50</td>
<td>1.81</td>
<td>0.68</td>
<td>1.13</td>
</tr>
<tr>
<td>Pt(411)</td>
<td>0.50</td>
<td>1.80</td>
<td>0.35</td>
<td>1.45</td>
</tr>
<tr>
<td>Pt(511)</td>
<td>0.67</td>
<td>1.81</td>
<td>0.31</td>
<td>1.49</td>
</tr>
</tbody>
</table>
S4. Ab initio atomistic thermodynamics

S4.1. Theory behind ab initio atomistic thermodynamics

Although DFT methods give a good estimate for a large set of physical quantities, its use is strictly only valid at \( T = 0 \text{ K} \) and \( p = 0 \text{ atm} \). A combination of DFT calculations and thermodynamics gives a better result for the value of these properties at different thermodynamic conditions. This approach can be used to compute the different surface energies for a particular arrangement and coverage of adsorbates, at different conditions of temperature and pressure, or concentration (in the case we were dealing with solutions).

In order to understand the effect of concentration of different adsorbed species on the stability and growth of Pt nanoparticle surfaces we employed ab initio atomistic thermodynamics. For this methodology, at constant temperature and pressure, the key magnitude is the Gibbs free energy, \( G(T, p) \).

If we consider the specific adsorption of HCl on Pt nanoparticles surfaces, the surface energy, \( \gamma_{\text{HCl}} \), is given by

\[
\gamma_{\text{HCl}} = \gamma_s + \Delta \gamma = \gamma_s + \frac{\Delta G}{A}
\]

where \( \Delta G \) stands for the change of the Gibbs free energy. This term can be written as

\[
\Delta G(T, p) = G_{\text{Pt-HCl}}(T, p) - G_{\text{Pt}}(T, p) - G_{\text{HCl}}(T, p)
\]

Here, \( G_{\text{Pt-HCl}}(T, p) \), \( G_{\text{Pt}}(T, p) \) and \( G_{\text{HCl}}(T, p) \) are the Gibbs free energies of HCl-covered Pt surfaces, clean Pt surfaces and HCl molecules, respectively. We present the formulation in terms of the pressure as done, normally, in the field of heterogeneous catalysis. The first contribution, \( G_{\text{Pt-HCl}} \) reads as

\[
G_{\text{Pt-HCl}}(T, p) = E_{\text{Pt-HCl}}^{\text{DFT}} + pV - TS + ZPVE_{\text{Pt-HCl}}
\]

where \( E_{\text{Pt-HCl}}^{\text{DFT}} \) is the energy obtained from DFT calculations for the HCl-covered Pt system, \( V \) is the system volume, \( S \) the entropy of the system, and \( ZPVE_{\text{Pt-HCl}} \) is the calculated zero-point vibrational energy. The \( pV \) contribution can be neglected for the bulk since its value is very small as
compared to the rest of terms. The term \( TS \) was neglected for the surface while for the HCl molecule we have taken the value from ref 9. Going back to eq 6, the second term, \( G_{pt} (T, p) \) was directly estimated from the DFT calculated energy, \( E_{pt}^{DFT} \).

\[
\Delta G(T, p) = E_{pt-HCl}^{DFT} + ZPVE_{pt-HCl} - E_{pt}^{DFT} - G_{HCl}(T, p)
\]  

(8)

For the last term, \( G_{HCl} \), we computed it from the HCl chemical potential, \( \mu_{HCl} \). Since we are dealing with a liquid environment, we can replace the pressure, \( p \), by the concentration, \( c \), of HCl.

\[
G_{HCl}(T, c) = n\mu_{HCl}(T, c)
\]  

(9)

with

\[
\mu_{HCl}(T, c) = E_{HCl}^{DFT} - TS_{HCl}(T, c^0) + ZPVE_{HCl} + RT\ln \frac{c}{c^0}
\]  

(10)

Here, \( n \) stands for the number of adsorbed HCl molecules, \( R \) is the gas constant, \( T \) equals 298 K and \( c^0 = 1 \) M. Now, with the estimations for \( G_{pt-HCl} \), \( G_{pt} \), and \( G_{HCl} \), and changing the pressure by the concentration in any of these terms, eq 5 can be written as

\[
\gamma_{HCl} = \gamma_s + \frac{1}{A} \left( E_{pt-HCl}^{DFT} + ZPVE_{pt-HCl} - E_{pt}^{DFT} - n \left[ E_{HCl}^{DFT} - TS_{HCl}(T, c^0) + ZPVE_{HCl} + RT\ln \frac{c}{c^0} \right] \right)
\]

\[
= \gamma_s + \frac{1}{A} \left( BE_{HCl} + ZPVE_{pt-HCl} - n \left[ -TS_{HCl}(T, c^0) + ZPVE_{HCl} + RT\ln \frac{c}{c^0} \right] \right)
\]  

(11)

With eq 11, we can now calculate the different Pt surface energies as a function of HCl concentration for each coverage.
S4.2. Linear fitting data

The surface energies, $\gamma_{HCl}$, obtained from the linear fitting are summarized in Table S5 at room temperature for a range of experimentally relevant HCl concentrations.

Table S5 Surface energies for the HCl-covered surfaces ($\gamma_{HCl}$), as a function of the HCl concentration, expressed as percentage (%) and molarity (M). For clarity, we also provide the values for ln($c/c^0$) in the range used in Fig. 2 in the main text.

<table>
<thead>
<tr>
<th>%</th>
<th>$c_{HCl}$</th>
<th>ln($c/c^0$)</th>
<th>100</th>
<th>110</th>
<th>111</th>
<th>211</th>
<th>311</th>
<th>411</th>
<th>511</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.16</td>
<td>-1.82</td>
<td>0.77</td>
<td>1.07</td>
<td>1.20</td>
<td>1.19</td>
<td>1.11</td>
<td>1.36</td>
<td>1.08</td>
</tr>
<tr>
<td>1</td>
<td>0.32</td>
<td>-1.13</td>
<td>0.75</td>
<td>1.06</td>
<td>1.18</td>
<td>1.18</td>
<td>1.09</td>
<td>1.35</td>
<td>1.06</td>
</tr>
<tr>
<td>10</td>
<td>3.24</td>
<td>1.18</td>
<td>0.69</td>
<td>1.02</td>
<td>1.11</td>
<td>1.13</td>
<td>1.02</td>
<td>1.29</td>
<td>0.99</td>
</tr>
<tr>
<td>15</td>
<td>4.86</td>
<td>1.58</td>
<td>0.68</td>
<td>1.01</td>
<td>1.10</td>
<td>1.12</td>
<td>1.00</td>
<td>1.28</td>
<td>0.98</td>
</tr>
<tr>
<td>25</td>
<td><strong>8.11</strong></td>
<td><strong>2.09</strong></td>
<td><strong>0.67</strong></td>
<td><strong>1.00</strong></td>
<td><strong>1.08</strong></td>
<td><strong>1.11</strong></td>
<td><strong>0.99</strong></td>
<td><strong>1.27</strong></td>
<td><strong>0.96</strong></td>
</tr>
<tr>
<td>37</td>
<td>12.10</td>
<td>2.48</td>
<td>0.66</td>
<td>0.99</td>
<td>1.07</td>
<td>1.10</td>
<td>0.97</td>
<td>1.26</td>
<td>0.95</td>
</tr>
<tr>
<td>43</td>
<td>13.95</td>
<td>2.64</td>
<td>0.66</td>
<td>0.99</td>
<td>1.07</td>
<td>1.10</td>
<td>0.97</td>
<td>1.25</td>
<td>0.95</td>
</tr>
<tr>
<td>50</td>
<td>16.22</td>
<td>2.79</td>
<td>0.65</td>
<td>0.99</td>
<td>1.06</td>
<td>1.09</td>
<td>0.96</td>
<td>1.25</td>
<td>0.94</td>
</tr>
<tr>
<td>60</td>
<td>19.46</td>
<td>2.97</td>
<td>0.65</td>
<td>0.99</td>
<td>1.06</td>
<td>1.09</td>
<td>0.96</td>
<td>1.24</td>
<td>0.94</td>
</tr>
<tr>
<td>70</td>
<td>22.70</td>
<td>3.12</td>
<td>0.64</td>
<td>0.98</td>
<td>1.05</td>
<td>1.09</td>
<td>0.95</td>
<td>1.24</td>
<td>0.93</td>
</tr>
<tr>
<td>80</td>
<td>25.95</td>
<td>3.26</td>
<td>0.64</td>
<td>0.98</td>
<td>1.05</td>
<td>1.08</td>
<td>0.95</td>
<td>1.24</td>
<td>0.93</td>
</tr>
<tr>
<td>90</td>
<td>29.19</td>
<td>3.37</td>
<td>0.64</td>
<td>0.98</td>
<td>1.05</td>
<td>1.08</td>
<td>0.95</td>
<td>1.23</td>
<td>0.92</td>
</tr>
<tr>
<td>100</td>
<td>32.43</td>
<td>3.48</td>
<td>0.63</td>
<td>0.98</td>
<td>1.04</td>
<td>1.08</td>
<td>0.94</td>
<td>1.23</td>
<td>0.92</td>
</tr>
</tbody>
</table>

The nanoparticle morphology derived from the Wulff construction shown in the inset of Fig. 2 in the main text was obtained using the surface energies at an experimental HCl percentage in the water phase of the 25%\textsuperscript{10} (these data are shown in bold in Table S5).
S5. Pitting values

**Fig. S2** DFT-calculated configuration of the Pt$_{365}$ nanoparticle covered by 119 HCl molecules. The positions where the pitting can take place are highlighted with a shaded square area (facet), solid lines (edge), and shaded circles (corner).

**Table S6** Reaction energies for the adsorption (+1Pt) and elimination (-1Pt) of a Pt atom at different positions: facet, edge and corner with respect to the isolated Pt atom.

<table>
<thead>
<tr>
<th>Structure</th>
<th>+1Pt Facet (eV)</th>
<th>-1Pt Facet (eV)</th>
<th>-1Pt Edge (eV)</th>
<th>-1Pt Corner (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$_{365}$</td>
<td>-4.43</td>
<td>5.37</td>
<td>4.64</td>
<td>3.62</td>
</tr>
<tr>
<td>Pt$<em>{365}$(HCl)$</em>{119}$</td>
<td>-4.63</td>
<td>4.17</td>
<td>4.16</td>
<td>5.11</td>
</tr>
</tbody>
</table>
S6. Geometrical model for the formation of concave structures

S6.1. Nanoparticle exposed surface and volume

A complementary method to DFT calculations to explain how concave structures are formed from a nanocube is the use of a geometrical approach. This methodology involves the intersection of the cube with a solid such that its surface planes correspond to the concave facets of the octapod-like structures observed experimentally. The point where the intersection starts is crucial to obtain the desired concave structures. Although not shown here, we have analyzed in detail how the final structures would look like if the pitting occurred at three different points in the cube: the (i) corners, (ii) face centers, (iii) edge centers. In this case, the only way to obtain octapods with sharp vertices involves the pitting occurring at the face centers and towards the center of the cube. In this section, we describe the process that results in the formation of octapod-like structures using plane geometry equations.

The first step in our model is to consider a set of tetragonal pyramids, whose faces are made of \{hll\} planes, that intersect each of the faces of a cube with side length \(a\) (see Fig. S3).

![Diagram showing the intersection of a tetragonal pyramid with a cube](image)

**Fig. S3** Concave structures exhibiting \{hll\} planes can be viewed as the intersection between a cube and a tetragonal pyramid made of \{hll\} planes that is inserted into each \{100\} cube face.

In order to obtain the total surface area we consider a parameter \(\delta\) that controls the depth at which the tetragonal pyramid is excavated out in each \{100\} plane. As shown in Fig. S4, where we focus on the (100) face of the cube (\(y - z\) plane), \(\delta\) is measured from the edge of each face and then,
there exist two different situations: (i) \(-a/2 < \delta \leq 0\) and (ii) \(0 \leq \delta \leq a/2\). When \(\delta = a/2\), the resulting structure is an octapod (Fig. S4 d).

Fig. S4 Concave structures resulting from the intersection between a cube (green) of side length \(a\) and a tetragonal pyramid composed of \(\{hll\}\) planes (red) in the \(y-z\) plane (\(x\) axis pointing towards the (100) plane). The gray dashed line in the bottom figures corresponds to the intersection between the tetragonal pyramid with the plane \(x = a/2\). The parameter \(\delta\) is measured from the edge of each face. Top figures (a,b) correspond to the case \(-a/2 < \delta \leq 0\) (\(\delta = 0\) in Fig. b) while bottom figures (c-d) to \(0 \leq \delta \leq a/2\).
The surface area of our concave nanoparticle can be calculated from surface integrals. If we have a surface $S$ defined by an equation $f(x, y, z) = c$, with $c$ being a constant, and $R$ is the projection of $S$ onto a closed and bounded plane, then,

$$S = \iint_R \frac{|\nabla f|}{|\nabla f \cdot \hat{p}|} dA$$  \hspace{1cm} (12)

where $\nabla f$ is the gradient of $f$, $\hat{p}$ is a unit vector perpendicular to $R$, and $dA$ is a differential of area on $R$. If we focus on the (100) plane ($\hat{p} = (1,0,0)$), the equations for the four \{hll\} planes shown in red in Fig. S4 are given by

$$\begin{align*}
    hx + ly - lz + \frac{a}{2} (l - h) + \delta l &= 0 , \quad (x > 0, y < 0, z > 0) \\
    hx - ly - lz + \frac{a}{2} (l - h) + \delta l &= 0 , \quad (x > 0, y > 0, z > 0) \\
    hx + ly + lz + \frac{a}{2} (l - h) + \delta l &= 0 , \quad (x > 0, y < 0, z < 0) \\
    hx - ly + lz + \frac{a}{2} (l - h) + \delta l &= 0 , \quad (x > 0, y > 0, z < 0)
\end{align*}$$  \hspace{1cm} (13)

Here, for any of the four planes with equation $f(x, y, z)$, the term $\frac{|\nabla f|}{|\nabla f \cdot \hat{p}|}$ can be written as follows

$$\frac{|\nabla f|}{|\nabla f \cdot \hat{p}|} = \frac{\sqrt{h^2 + 2l^2}}{h}$$  \hspace{1cm} (14)

This result is independent of $y$ and $z$ and, then, we can pull it out from the integral in eq 12. If we call $R'$ the portion in the (100) plane such that $x > 0, y > 0, z > 0$ with $z > y$, and we consider the symmetry of the nanoparticles, the surface area, $S_{hll}$, of the exposed \{hll\} planes can be calculated as

$$S_{hll} = \frac{8\sqrt{h^2 + 2l^2}}{h} \iint_{R'} dA = \frac{8\sqrt{h^2 + 2l^2}}{h} S'$$  \hspace{1cm} (15)
where $S' = \iint_{R'} dA$. The surface area of the (100) face, $S_{100}$, if any, is simply

$$S_{100} = a^2 - 8S'$$  \hspace{1cm} (16)

Then, the total surface area, $S_{tot}$, of each side of the nanoparticle is

$$S_{tot} = S_{hll} + S_{100}$$  \hspace{1cm} (17)

In the following, we calculate $S_{hll}$ for $\delta < 0$ and $\delta > 0$.

- **Case 1: $-a/2 \leq \delta \leq 0$**

In this case, $R'$ is defined as

$$R' = \left\{ \begin{array}{l}
y \leq z \leq \frac{a}{2} + \delta - y \\
0 \leq y \leq \frac{1}{2} \left( \frac{a}{2} + \delta \right)
\end{array} \right\}$$  \hspace{1cm} (18)

For clarity we also show this region in Fig. S5 a.

![Integration region $R'$ for $\delta < 0$ (a) and $\delta > 0$ (b).](image)

**Fig. S5** Integration region $R'$ for $\delta < 0$ (a) and $\delta > 0$ (b).
The surface area of $R'$, called $S'$, is calculated straightforwardly

$$
S' = \int_{0}^{\frac{a}{2} + \delta} \int_{\frac{a}{2} + \delta - y}^{\frac{a}{2} + y} dz dy = \int_{0}^{\frac{a}{2} + \delta} \left( \frac{a}{2} + \delta - 2y \right) dy = \frac{1}{4} \left( \frac{a}{2} + \delta \right)^2
$$

(19)

Then, using eq 15 we calculate $S_{\text{hill}}$ as

$$
S_{\text{hill}} = \frac{2\sqrt{h^2 + 2l^2}}{h} \left( \frac{a}{2} + \delta \right)^2
$$

(20)

Here, $S_{100}$ is computed using eq 16.

- **Case 2: $0 \leq \delta \leq a/2$**

The region $R'$ is now defined as (see also Fig. S5 b)

$$
R' = \left\{ \begin{array}{l}
y \leq z \leq \frac{a}{2} + \delta - y \\
0 \leq y \leq \frac{a}{2} + \delta
\end{array} \right\} - \left\{ \begin{array}{l}
\frac{a}{2} \leq z \leq \frac{a}{2} + \delta - y \\
0 \leq y \leq \delta
\end{array} \right\} \\
- \left\{ \begin{array}{l}
ly + \frac{a(h - l) - 2\delta l}{2(h - l)} \leq z \leq \frac{a}{2} \\
0 \leq y \leq \delta
\end{array} \right\}
$$

(21)

The second and third term correspond to the blue and white triangles shown in Fig. S5 b, respectively. The surface area $S'$ can be calculated as for the previous case ($\delta < 0$), but now we need to subtract the area of both triangles. The base and height of the blue triangle are equal to $\delta$, whereas for the white triangle they equal $\delta$ and $d = \delta l/(h - l)$, respectively. Then,

$$
S' = \frac{1}{4} \left( \frac{a}{2} + \delta \right)^2 - \frac{\delta^2}{2} - \frac{\delta^2 l}{2(h - l)} = \frac{1}{4} \left( \frac{a}{2} + \delta \right)^2 - \frac{\delta^2 h}{2(h - l)}
$$

(22)
For $S_{100}$, in the case $\delta > 0$, we can not use $S'$ as defined in eq 22 as, here, we should not consider the area of the white triangle. Then,

$$S_{100} = a^2 - \left[2 \left(\frac{a}{2} + \delta\right)^2 - 4\delta^2\right]$$

(23)

As done before, we just need to consider the symmetric shape of the nanoparticle using eq 15 to compute $S_{hil}$,

$$S_{hil} = \frac{\sqrt{h^2 + 2l^2}}{h} \left[2 \left(\frac{a}{2} + \delta\right)^2 - \frac{4\delta^2h}{(h - l)}\right]$$

(24)

Due to the fact that both eqs 20 and 24 are equal except for the last term in eq 24, we can introduce a Heaviside step function, $\theta(\delta)$ and write $S_{hil}(\delta)$ as follows

$$S_{hil}(\delta) = \frac{\sqrt{h^2 + 2l^2}}{h} \left[2 \left(\frac{a}{2} + \delta\right)^2 - \frac{4\delta^2h}{(h - l)} \theta(\delta)\right]$$

(25)

where $\theta(\delta)$ is given by

$$\theta(\delta) = \begin{cases} 1, & \delta > 0 \\ 0, & \delta \leq 0 \end{cases}$$

(26)

Fig. S6 shows $S_{tot}$ as a function of $S_{100}$ for $h = 3$, $l = 1$ and $a = 1.0$ (in arb. units).
Fig. S6 Total surface area, $S_{\text{tot}}$, of each side of the nanoparticle as a function of the area of the (100) face, $S_{100}$, for the case $h = 3$, $l = 1$, and $a = 1$ (arb. units).

In order to compute the surface-area-to-volume ratio we have calculated the volume, $V$, of the nanoparticle as a function of $\delta$. In this case, $V$ also has a different functional form depending on the sign of $\delta$. We do not provide here the whole set of equations used to compute $V$ but just give its final functional form.

For $\delta \leq 0$ we have:

$$V_{\delta \leq 0} = a^3 - \frac{l}{2h} (a + 2\delta)^3$$  \hspace{1cm} (27)

For $\delta \geq 0$ we have:

$$V_{\delta \geq 0} = a^3 - \left[ \frac{l}{2h} \left( \frac{a(h - l) - 2\delta l}{h - l} \right)^3 + \frac{3\delta l}{(h - l)^3} (a(h - l) - 2\delta l)^2 + \frac{8l^2\delta^3}{(h - l)^2} + \frac{12\delta^2 lh}{(h - l)^2} \left( \frac{a}{2} - \delta \right) + \frac{8\delta^3 lh(h - 2l)}{(h - l)^3} \right]$$  \hspace{1cm} (28)

When $\delta = 0$ both eqs 27 and 28 yield the same value $V_{\delta = 0} = a^3 (1 - l/2h)$. 
Another result to point out is that we cannot have octapods for any combination of the Miller indices such that $h > l$ and $l = k$. This result can be easily obtained if we look at eq 13 for any of the planes and we set $\delta = a/2$. In this case, there should exist some thickness, $x_0$, in the $x$-axis at the point where the four planes intersect each other (at $y = 0$ and $z = 0$, see Fig. S4 d). Looking at any of the four planes, and setting $\delta = a/2$, we have the following result

$$x_0 = \frac{(h - 2l) a}{h} \frac{1}{2}$$

which means that we can only have octapod-like concave nanoparticles when $h > 2l$. Then, (311), (411) and (511) facets can be present in octapods, but not {211} or {433} planes, a result that agrees with experimental observations where mainly (311) and (411) faces have been reported.

**S6.2. Relationship of $\delta$ with the HCl concentration**

The parameter $\delta$ is a function of the concentration $c$ of HCl. The concentration at which the nanoparticles adopt the different shapes can be determined experimentally from TEM measurements and then one can assess the functional form of $\delta(c)$. In the case of $\delta$ depending linearly on $c$:

$$\delta = -\frac{a}{2} + \frac{a}{c_2 - c_1}(c - c_1)$$

where $c_1$ stands for the concentration at which nanocubes are formed, while $c_2$ corresponds to the value at which octapods are observed. At $c = (c_2 + c_1)/2$ the situation is that shown in Fig. S4 b ($\delta = 0$). For eq 30 to be true, the side length of the nanoparticle should be equal to $a$ during the etching process. The parameter $\delta$ can also depend on $c$ as a power law $\delta(c) \propto (c - c_1)^{\alpha}$ with $\alpha > 1$ or $\delta(c) \propto (c/c_1)^{-\beta}$ with $\beta > 1$. Then, once the dependence $\delta(c)$ is determined, one just need to enter a value for $c$ in eq 30 in the range $[c_1, c_2]$ to calculate $\delta$ and then the total nanoparticle exposed surface and volume would be obtained through eqs 17, 23, 25, 27 and 28.
References


