8. Caption of Supplementary Information

Figure IS1: Representative snapshots for a truncated octahedron nanoparticle. The seed or core are symbolized by yellow spheres (N_A=2951) and the adsorbate or shell with purple spheres. We use the follow notation $core_{1925}@shell_{NB}$, where NB denote the number of B particles. The surface of this nanoparticle is formed by facets {100} and {111}, two kind of borders {111-111} and {100-111}, and 24 vertices. In the inset $core_{1925}@shell_{728}$ the adsorbate is deposited in the (111) facets. Each adatoms is linked with 6 lateral NNs (NN_{lat}) and 3 atoms of the seed (NN_{seed}). In the $core_{1925}@shell_{150}$, the adsorbate is deposited in the (100) facets, then NN_{lat} =4 and NN_{seed}=4. But in $core_{1925}@shell_{180}$ the adsorbate is deposited in borders {111-111} and {100-111}. In the first(second) case the adatoms is linked with NN_{lat} =6 (5) and NN_{seed} = 1(2). Finally in $core_{1925}@shell_{24}$ the adsorbate is deposited on the vertices where is linked NN_{lat} =5 and NN_{seed} = 1. The table resumes the coordination of this NP.

Figure IS2: Representative snapshots of simulations for a ICO-NP with *n*=7. a), b) and c) correspond to the three subplateaus formed in the first plateau, yielding a frustrated (√3x√3) structure. Is important note how the occupation of the vertices induces the filling of each facet. Note that even in b), which corresponds to a coverage where the (√3x√3) structure can cover all the surface, all vertices are not equivalent.

Figure SI3: Differential heat for several sizes of ICO-NPs. We observe that for *n*= 3, 6 and 9 only one step is visible at θ=1/3. However, for the other cases, multiple steps are observed. The inset shows a zoom of the first step.

Figure IS4: Isotherm for n =9 with $\delta E = 7.0$. A single plateau at θ=1/3 and three different plateaus at θ =2/3 are clearly observed. Black [white] dots denote sites which are occupied [empty]. The inset (a) shows a snapshot of the (√3 x √3) structure formed on the ICO. Inset (b) shows a snapshot corresponding to θ=0.667 (the middle plateau).The vacancy-particle symmetry is broken.

Figure SI5: a) Behavior of the isotherms of a tetrahedron (N_A=1771) and a decahedron (N_A=1442) for $\delta E = 7.0$. In both cases subplateaus are presents around characteristic coverages. b) Differential heats for the isotherms presented in a). Note in the latter the occurrence of steps in concordance with the behavior of isotherms.

Figure SI6: (Color online) a) Adsorption isotherms corresponding to a CO-NP with $N_A = 2057$. b) Normalized distribution of surface clusters at different chemical potentials, as marked in figure. Note the presence of monomers, trimers, tetramers, etc. on the surface of the NP.

Figure SI7: Compressibility as a function of chemical potential for a CO NP , with N_A=2057 for different adsorbate-adsorbate interaction energies. Like in the case of ICO-NPs, it is observed that the maxima are spread as δE increases. Submaxima are observed.

Figure SI8: (Color online) a) Mean square fluctuations as a function of chemical potential, corresponding to simulations with a truncated octahedron. b) Differential heat as a function of coverage degree.