Appendix – Supporting Information

S1 TEM characterization of the Pt cubic nanoparticles.

Figure S1. TEM images of Pt nanoparticles obtained after cathodic treatment in 10M NaOH. AC voltage –10 to 0 V, $v = 100$ Hz. The size bar in the figure is 10 nm.

S2 Nitrite reduction as a characterization tool for Pt nanoparticles.
Having shown the peculiar surface-sensitivity of nitrite reduction, it could be envisaged to use this reaction as an ancillary characterization method for Pt nanoparticles. A proof-of-concept example is shown in figure S1, which shows the characterization of nanoparticles prepared with the colloidal route. Panels A and C show the blank voltammetric profile of two samples of colloidal nanoparticles.

The blank voltammetry in Figure S2A is distinctive of “cuboctahedral” (or “truncated octahedral”) nanoparticles [1], featuring large, well-oriented (111) sites, associated with the voltammetric signal at 0.5 V typical of sulfate/bisulfate adsorption [2], along with the voltammetric peaks characteristic of narrow and long (100) sites. It can be seen (Figure S2B) that nitrite reduction is able to “deconvolute” the complexity of the nanoparticle surface, highlighting the contribution of every site to this reaction. Specifically, the presence of large and well-ordered (111) domains give rise to the shoulder at 0.27 V in Figure S2B, merged with the broader main peak, which can be associated with nitrite reduction at (111) terraces, as demonstrated by previous experiments with single-crystals [3-5] (see also Figure 2). The main peak, typical of nitrite reduction to ammonia at (100) sites, evidences the presence of a certain percentage of (100) sites. On the other hand, the small peak associated with N₂ evolution signals that these nanoparticles also feature large (100) facets, corroborating the evidence of the blank voltammetry (Figure S2A). Figure S2C shows a second sample prepared following a colloidal synthetic route: in this case, the blank voltammetry displays most of the features also visible in Figure S2A but the peak associated with (100) narrow terraces has a larger relative magnitude (with respect to the (110) peak, which is less sharp than in Figure S2A) and the (111) (bi)sulfate adsorption feature is weaker. Nitrite reduction can effectively highlight these peculiarities: the shoulder related to nitrite reduction at (111) sites is very weak and barely appreciable in Figure S2D, while the peaks related to (100) domains and defects predominate in the voltammogram.
**Figure S2** Panels A and C: blank voltammograms in 0.5 M H$_2$SO$_4$ of two nanoparticle samples prepared with the colloidal method, $v = 50$ mV s$^{-1}$. Panels B and D: voltammetric profiles for the reduction of 2 mM NaNO$_2$ in 0.1 M NaOH, $v = 20$ mV s$^{-1}$. Panels A-B and C-D refer to the same nanoparticle sample.

**Bibliography**


