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On the quality and stability of preferentially oriented (100) Pt nanoparticles: an electrochemical insight

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Abstract

Previous knowledge shed by single crystal electrochemistry path the way to obtain better catalysts aiming fuel cell purposes. In this sense, tailoring shape-controlled nanoparticles has been a strategy followed over the past years to optimize the activity, selectivity and stability of electrocatalytic surface sensitive reactions by maximizing the exposure of certain facets of the nanocatalyst. In the present paper, preferentially oriented (100) nanoparticles synthesized by different methodologies have been electrochemically characterized and compared. The voltammetric profile of these cubic nanoparticles has also been compared with different platinum single crystal stepped surfaces, showing a singular fitting to the characteristic response of Pt(510). Subtle changes on the surface structure of platinum nanocubes due to surface degradation upon storage time in aqueous solution are pointed out in this work. The characteristic fingerprints of platinum surfaces and CO oxidation profiles have demonstrated to be powerful surface probes for the *in situ* detection of these minor structural reorganizations.

Keywords: Surface structure; Pt single crystal electrodes; Pt nanocubes; *In situ* characterization; Structural Stability.

1. Introduction

More than three decades of platinum (Pt) single crystal electrochemistry have clearly pointed out the potentiality of these tools for studying, in a simplified way, the effect of surface structure on a given electrocatalytic reaction [1]. In this sense, many works using single crystal electrodes have been carried out aiming a deeper understanding of the electrochemical reactivity of relevant catalytic reactions at a molecular level. However, for practical purposes (i.e. in a polymer electrolyte membrane fuel cell (PEMFC)) electrocatalysts are normally used as small particles of nanometer sizes. When these nanoparticles are synthesized with a particular shape, they can have a well-defined surface structure. In fact, the shape of a nanoparticle anticipates which facets will be present at its surface due to the intrinsic correlation between the shape and the surface structure of a nanoparticle [2, 3]. Therefore, shape-controlled nanoparticles are the ideal tools to apply all the knowledge obtained from single crystal electrodes to practical purposes [4]. For instance, better catalysts with higher activity and selectivity can be potentially developed by modulating the morphology of the nanoparticles [5-12].

Over the past years, significant progress has been achieved in obtaining size and shape-controlled metal nanoparticles, with increasing quality of the tailored nanocrystals [5, 13-16]. The preparation of shape-controlled nanoparticles requires in most of the cases the use of surface-stabilizing agents that adsorb during their nucleation and growth to induce the desired geometry. Since the flame-annealing protocol cannot be applied to nanoparticles, a specific decontamination procedure (different for each particular synthetic method) must be applied in order to completely remove the adsorbed species present at the surface of the synthesized nanoparticles [16]. Unfortunately, when this cleaning step is not properly made, the electrocatalytic activity of the nanoparticles is affected in a non-controlled way, by either the surfactant or its degradation products. In both cases, the surfactant layer structure and composition of the nanoparticles will depend on the storage environments and consequently reproducible and comparable results from different laboratories cannot be reached. Additionally, the surface cleaning step must be performed without perturbing the initial surface structure of the nanoparticles. In this regard, it is important to recall that, from an electrocatalytic point of view, the shape of the nanoparticles is not the key parameter but their real surface structure at atomic level [17-19].

One of the main drawbacks of shaped nanoparticles is their compromised stability. In this regard, when they are stored for a long time or are subjected to improper pretreatment protocols, surface oxidation and subsequent modification can be observed. Clear cases are reported for Pd nanocrystals, whose shape stability in the presence of polyvinylpyrrolidone (PVP) was found to follow the trend: cubic < cuboctahedral < octahedral ~ concave cube [20]. In the same way, it was previously reported on Pt single crystal electrodes that two-dimensionally ordered (100) terraces are very susceptible to surface reconstruction [21]. Consequently, nanoparticles with {100} facets, i.e. Pt nanocubes (NCbs), are the most vulnerable to suffer from surface degradation.

Comparison of voltammetric profiles of single crystal electrodes in a well-defined test electrolyte with data from surface sensitive techniques has allowed characterizing the topography of these platinum single crystals by using this simple electrochemical technique [22, 23]. In this work, we aim to compare the voltammetric response of Pt NCbs obtained by different synthetic routes, relating them to the characteristic behavior of Pt(100) electrode and its stepped surfaces. In addition, we will demonstrate by cyclic voltammetry the progressively etching of cubic Pt nanoparticles during different stages of their lifetime, pointing out the great valiance of this *in situ* technique to identify subtle changes on the surface structure of shaped-nanocrystals.

2. Experimental

Pt single crystal electrodes were prepared following standard procedures described elsewhere [24]. Pt(100) and its vicinal surfaces Pt(S)[n(100)×(110)], with Miller indices Pt(n 1 0), where n is the number of terrace rows, were used as working electrodes. Also a Pt(320) electrode (Pt(S)[n(110)×(100)]) was used. Before each experiment, the single crystal electrodes were flame-annealed, cooled down in a reductive atmosphere (H_2 + Ar in a 1:3 ratio) and quenched in ultrapure water in equilibrium with this atmosphere before transferring to the electrochemical cell.

Synthesis of Pt shaped nanoparticles are described in previous contributions [5, 13-16, 25]. Prior to the electrochemical performance, the surfaces of the nanocatalysts were decontaminated following the specific procedure for each synthetic methodology. A droplet ranging from 1 to 3 μL of the solution containing the nanoparticles was deposited on a disc of polycrystalline gold substrate and dried under an Ar atmosphere. By using this procedure, typically around 10^{11} nanoparticles per cm^2 are deposited. Before each experiment, the gold collector was mechanically polished with alumina and rinsed with ultrapure water to eliminate the nanoparticles from previous experiments.

The electrochemical characterization of the different Pt surfaces was performed at room temperature by cyclic voltammetry at a sweep rate of 50 mV s^{-1} in Ar (Air Liquide, N50) saturated 0.5 M H_2SO_4 (96 %, Merck, Suprapur®), 0.1 M $HClO_4$ (70 %, Merck, Suprapur®) and 0.1 M NaOH (99.99 %, Merck, Suprapur®) solutions. A three electrode electrochemical cell was used with a Pt wire as a counter electrode and a reversible hydrogen electrode (RHE), connected to the cell through a Luggin capillary, as reference electrode. The electrode potential was controlled using a PGSTAT30 AUTOLAB system, and an EG&G PARC 175 signal generator in combination with an eDAQ EA 161 potentiostat and currents were recorded using an eDAQ e-corder ED401 recording system.

To perform the adsorbed CO oxidation experiments, CO (g) was bubbled through the electrolyte at an admission potential of 0.05 V until complete blockage of the surface was reached, which was monitored by cycling the electrode between 0.05 and 0.35 V. After that, CO was removed from the solution by bubbling Ar for at least 15 min. CO-stripping voltammograms were registered at 20 mV s^{-1} to oxidize the CO molecules adsorbed on the surface in a single sweep.

Transmission electron microscopy (TEM) has been employed to investigate the shape of the nanoparticles. TEM experiments were performed with a JEOL, JEM 2010 microscope working at 200 kV. The sample was obtained by placing a drop of the dispersed solution onto a Formvar covered copper grid and evaporating it in air at room temperature. More than 300 nanoparticles from different parts of the grid were used to estimate the mean diameter and size distribution of the nanoparticles.

3. Results and Discussion

3.1. Surface structure's fingerprint

The electrocatalytic response of an electrode can be determined by the reactions undergone by the species adsorbed on its surface, the so-called *surface structure sensitive reactions*. From a fundamental point of view, anion co-adsorption plays a key role in the building of the adlayer, affecting the reactivity of the surface due to competition for the surface sites with other *structure sensitive processes*. In fact, hydrogen [26, 27] and many anions (hydroxyl [28, 29], sulfate [30-32], chloride [33, 34]…) have been demonstrated to specifically adsorb onto platinum surfaces given rise to characteristic responses. Thus, cyclic voltammograms in a given supporting electrolyte have been confidently used during many years as a surface characterization fingerprints for well-defined Pt(hkl) electrodes. **Figure 1A** shows the distinct responses of a Pt(100) electrode in the three most frequently used aqueous supporting electrolytes: 0.5 M H_2SO_4, 0.1 M $HClO_4$ and 0.1 M NaOH. It should be remarked that in all cases, the surface topography, e.g. wide two-dimensional domains of square sites, is the same, irrespectively of the test electrolyte used.

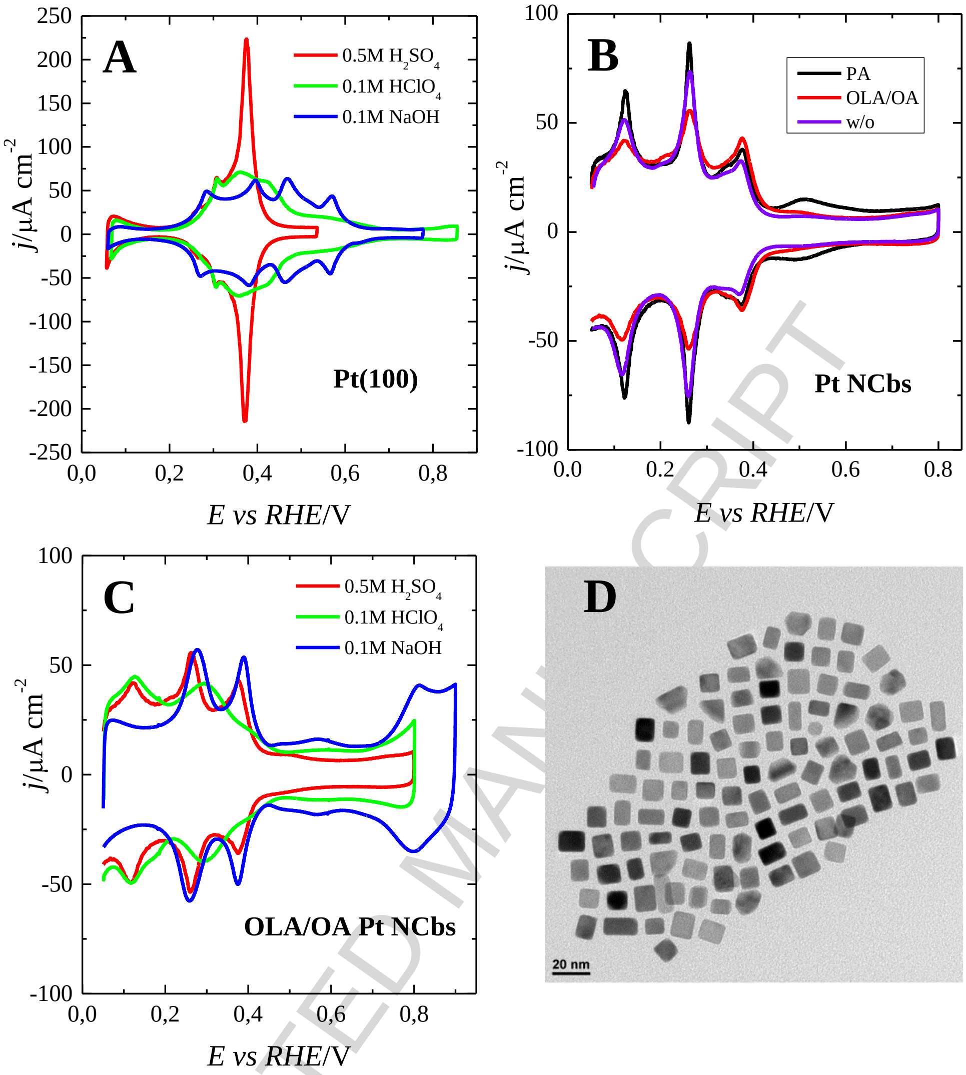

Figure 1. Characteristic cyclic voltammograms for (A) Pt(100) electrode and (B, C) Pt cubic nanoparticles in 0.5 M H_2SO_4 (red), 0.1 M $HClO_4$ (green) and 0.1 M NaOH (blue) media. Sweep rate, 50 mV s^{-1}. (B) Voltammetric response of Pt NCbs synthesized using different methodologies: PA (black), OLA/OA (red) and w/o (violet). (D) Representative TEM image of OLA/OA cubic nanoparticles.

As can be seen, the features of the voltammetric profile in sulfuric acid are sharper than in the other media. The specific adsorption of sulfate anions makes the so-called hydrogen adsorption/desorption states better defined than those observed in perchloric acid. On the other hand, the presence of four different contributions in alkaline medium indicates that the adsorption processes of hydrogen and OH are more complex in this supporting electrolyte due to competitive adsorption [35]. For this reason, it is more convenient to use sulfuric acid as the test solution for electrochemical characterization purposes, this statement being also valid for Pt nanoparticles.

In a further state, **figure 1B** shows the characteristic voltammetric responses of various samples of Pt NCbs synthesized following different proceedings: i) a colloidal method using sodium polyacrilate (PA) as capping agent, H_2PtCl_4 as metallic precursor and H_2 as reducing agent [5, 25]; ii) a high temperature process using the mixture oleylamine/oleic acid (OLA/OA) as solvent and capping agents, $Pt(acac)_2$ as metallic precursor and $W(CO)_6$ as reductant [13, 16]; and a water-in-oil (w/o) method in which K_2PtCl_6 is reduced with $NaBH_4$ in the presence of HCl [14] or H_2SO_4 [15], acting as surface modifiers. The mean size distribution of the nanoparticles were 8 ± 2, 11 ± 2 and 13 ± 1 nm, respectively. In all cases, the good definition and symmetry of the adsorption states are an indicative of the adequate surface cleanliness. Note that, regardless of the synthesis method used to prepare the Pt NCbs, comparable voltammetric profiles are obtained for nanoparticles with similar morphology, being the peak at 0.37 V (related to (100) wide terraces) the characteristic feature of Pt nanoparticles with (100) preferential orientation [25]. However, the subtle differences between the three samples reflect the different size and quality of the nanocrystals at atomic level. Therefore, the presence of better defined {100} facets on the NCbs can be in-situ evidenced by the relation between the peak at 0.37 V ((100) terraces) and those at 0.12 and 0.26 V ((110) and (100) defects or short domains, respectively). In addition, the feature at around 0.5 V, related to sulfate adsorption on (111) long domains, it is and indicative of highly truncation of the NCbs.

Within the various synthetic methodologies followed in our group to obtain Pt shaped nanoparticles, the procedure that uses OLA/OA as surfactant has demonstrated to lead to highly faceted nanocrystals of outstanding quality, as pointed out in **figure 1B**, yielding to ca. 90 % of cubic nanoparticles. What is more, the development of a specific cleaning protocol that preserves the surface structure of the nanoparticles synthesized by this method [16] has allowed further studies with this kind of electrocatalysts [18, 36, 37]. In this regard, **figure 1C** displays the fingerprint in the three aforementioned supporting electrolytes of the Pt NCbs obtained by the OLA/OA method. It is important to point out that, unlike to what described for Pt(100) single crystal electrode (**figure 1A**), the shape-controlled nanoparticles also exhibit characteristic profiles in the different aqueous media. The comparison with the voltammetric signals found on single crystal electrodes, however, allows the precise identification of the surface structure of the nanocatalysts without requiring microscopic imaging [38]. For sake of comparison, **Figure 1D** shows a representative TEM image of the nanoparticles analyzed in **figure 1C**, evidencing the consistency between the cubic shape of the nanocrystals (microscopic *ex situ* analysis) and the (100) preferential surface orientation observed electrochemically (voltammetric *in situ* analysis). It is also important to highlight that whereas in a TEM image is possible to analyze the shape of dozens or hundreds of nanoparticles, in the cyclic voltammogram of a small deposit of the same electrocatalyst the mean response of hundreds of millions of nanoparticles is acquired, which is a more realistic statistical result.

Certainly, the surface of the nanoparticles is much more complex than the ideal single crystal surfaces. Noble metal nanoparticles are constituted by a comparatively small number of atoms, which are atomically arranged following the structures present on the low-index crystal planes. However, due to their limited surface size, besides the presence of surface terraces (which are maximized in the case of shape-controlled nanoparticles), they also involve an important concentration of corner, edge and kink atoms, including surface atoms with low coordination number (CN) which may considerably influence their electrocatalytic activity [8]. Still, it is possible to establish surface correlations between nanoparticles and single crystal electrodes using single crystal stepped surfaces, where the density of defect sites (the steps) and its symmetry are deliberately controlled. In analogy with the unit stereographic triangle, there is also an intrinsic triangle that locates the crystal surface index and the shape of the nanoparticle [39]. Thus, the voltammetric response of Pt shaped nanoparticles can be mimicked by model stepped surfaces. **Figure 2** exemplifies these phenomena. **Figure 2A** displays the characteristic voltammetric behavior of Pt NCbs and some stepped surfaces vicinal to the (100) pole, named Pt(n10) or Pt(S)[n(100)×(110)], which are composed by (100) terraces with different length (n) separated by monoatomic (110) steps. It is possible to observe that, as the step density increases, the peak at 0.37 V (characteristic of (100) long domains) decreases to the detriment of an increase in the intensity of the peak at 0.26 V (related to (100) terrace borders or short domains). In the same way, the charge density below 0.2 V is larger for surfaces with higher density of (110) steps, becoming a well-defined peak at 0.12 V for the Pt(320) electrode (Pt(S)[n(110)×(100)]). In the case of Pt NCbs, the voltammogram displays these three features, followed by an almost constant double-layer contribution up to 0.8 V.

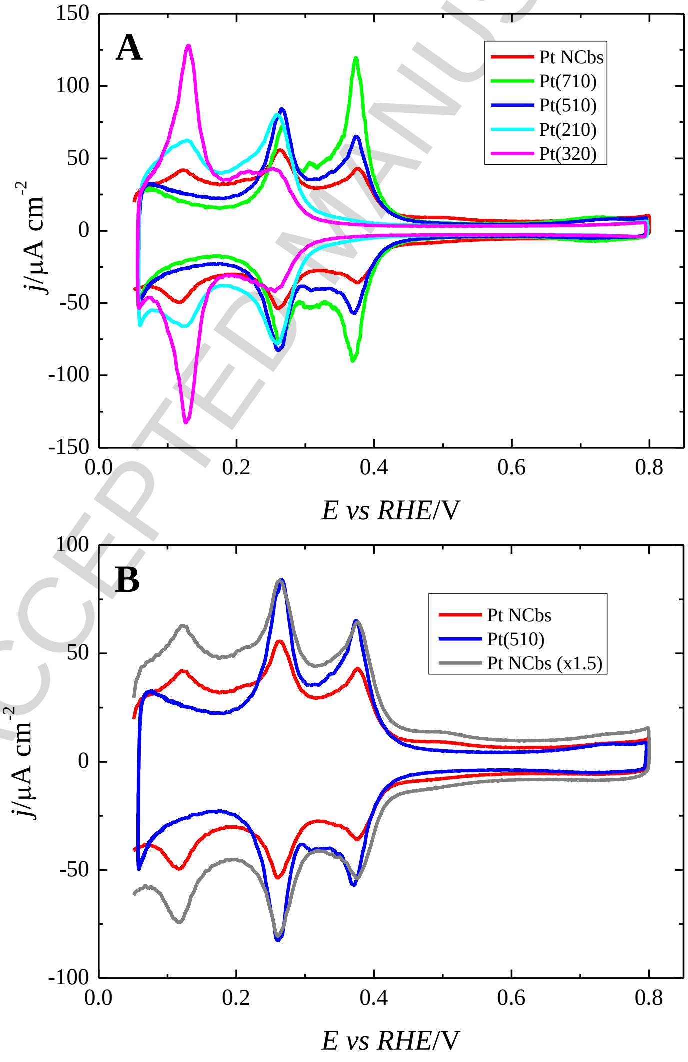

Figure 2. Comparison of the characteristic voltammetric profiles of (A) some stepped surfaces vicinal to the (100) pole with the representative response of Pt cubic nanoparticles, (B) Pt(510) and Pt NCbs, whose

current density has also been multiplied by 1.5 for relative intensity peak comparison. 0.5 M H_2SO_4, 50 mV s^{-1}.

Figure 2B compares the voltammetric profiles of Pt NCbs and the Pt(510) stepped surface single crystal electrode. As the Pt NCbs contains higher number of defects (in addition to the nanoparticles with irregular shape), the current density measured with the nanoparticles has been multiplied by 1.5 for a better comparison with the single crystal surface. As can be seen, the two main peaks fit with those of the single crystal. The results presented in this figure clearly point out the good correlation that can be established between single crystal electrodes and shaped nanoparticles. What is more, given the good overlapping between both voltammograms, it would be possible to argue that these cubic nanoparticles possess terraces of about five atoms width, since this is the number of atom rows in the terraces of Pt(510) electrode. This conclusion, however, should be taken cautiously: it is clear that the surface of the nanoparticles is limited by two finite lengths as in **figure 3** (the 3D model has been represented by using Vesta program [40]). Nevertheless, for a stepped single crystal electrode only the terrace length is finite (n) and this refers to the terrace atoms that are perpendicular to the steps, but the length of the terrace in the direction parallel to the step can be considered infinite. In this respect, for single crystals and nanoparticles the number of spatial restrictions is different and the resulting influence on the reactivity is far to be fully understood.

As pointed out, an ideal cubic nanoparticle is enclosed by low-index {100} facets, where the surface atoms have a CN of 8. The use of stabilizing agents allows obtaining nanocrystals with this faceted structure by preferentially adsorption onto specific surface orientations. However, for catalytic purposes, these growing assistants must be removed from the surface of the nanocatalysts prior to the electrochemical performance. This surface decontamination step can compromise the stability of the surface atoms, even inducing structural modifications, particularly when high interfacial potentials are reached [17]. In addition, it is not surprising that relatively low coordinated atoms present at the surface of NCbs tend to move towards a situation with lower surface energy. In this regard, the edges of NCbs are normally truncated, exposing {111} facets with higher CN (9). The adsorption of hydrogen on these small domains is responsible for a significant fraction of the adsorption charge exchanged in the potential range between the potential of zero total charge (pztc), around 0.28 V for cubic nanoparticles in sulfuric acid [41], and the beginning of hydrogen evolution (**figure 3**). This particular zone also involves the contribution of the charge under the peaks at 0.12, 0.28 and 0.37 V, as it was previously shown by peak deconvolution [38]. Moreover, anion adsorption takes place in relatively large (111) domains, giving rise to a typical feature around 0.5 V, characteristic of Pt nanooctahedra or truncated NCbs, but only hydrogen can adsorb at small domains with this compact orientation [42, 43]. On the other hand, (110) sites are placed in the intersection between two (111) and/or two (100) planes. In a cubic nanoparticle, (110) sites are exposed when its edges are beveled, as shown in **figure 3**. It is worth to mention that the surface sites distribution depends not only on the synthetic route and decontamination protocol used to prepare the nanocatalysts, but also on the particle size, temperature and chemical environment in which the nanocrystals are employed or stored, and can be modified by the applied potential under working conditions [44]. Therefore, the resulting electrocatalytic activity will be dominated by the final atomic arrangement at the surface of the nanoparticles, among other determining factors such as agglomeration or influence of the supporting material on the surface rearrangements. Although this analysis showing the heterogeneous surface complexity of a nanoparticle such as that of **figure 3**, we should consider that other nanoparticles with a different shape can result in every particular synthetic protocol. This is not a strange situation in chemistry: these nanoparticles with other shape are like the side products found in inorganic or organic synthesis, which generally never achieve the 100 % yield in the desired product. Obviously, the platinum atoms present in these other nanoparticles (some of them could be identified in **figure 1D**) will also contribute to the overall electrochemical response.

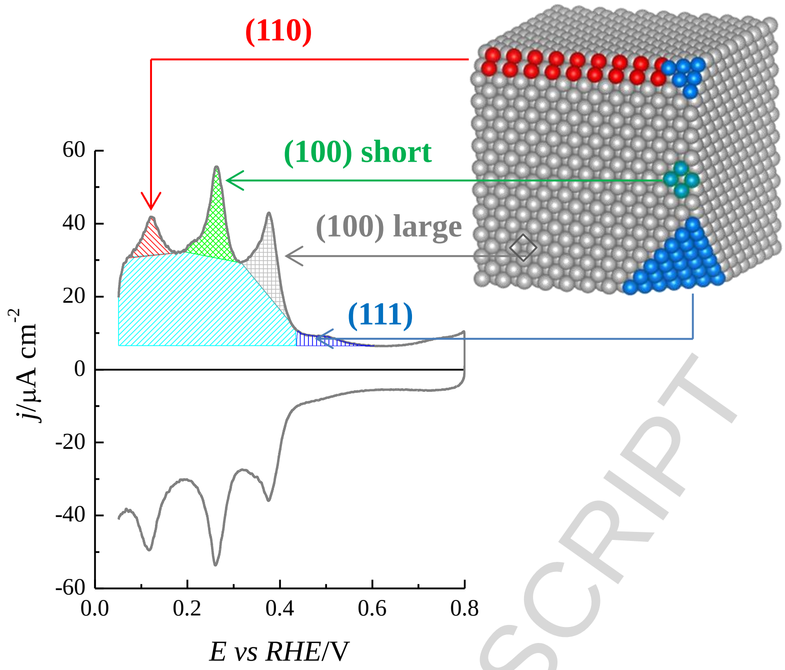

Figure 3. Characteristic voltammetric profile and atomic model of (100)-preferentially oriented Pt nanoparticles in 0.5 H_2SO_4, showing beveled and truncated edges and its correspondence with the different voltammetric features.

3.2. Surface degradation and stability of Pt NCbs

From theoretical calculations was concluded that the surface energy of Pt(110) is higher than that of Pt(100) [45]. Therefore, dodecahedral nanocrystals (enclosed by {110} facets) should display the worst structural stability. However, atomistic simulations have shown that nanoparticles with this morphology present better stability than the cubic ones [39], inferring that surface energy calculated in vacuum conditions is not the only factor that determines the stability of polyhedral nanocrystals [3]. In particular, it is well documented the effect of oxygen adsorption at high temperature in the surface disordering of Pt(100) electrodes [22]. In the present work, the stability of Pt NCbs synthesized by the OLA/OA method has been studied over a wide period of time. Cyclic voltammetry has been used to monitor the changes on the surface of the nanocatalysts. The initial voltammetric profile was recorded as soon as the nanoparticles were synthesized and decontaminated [16] (**figure 4A**, black line). Then, the clean nanoparticles were stored in an aqueous solution (MilliQ quality water) at room temperature, and tested after 2 and 3 weeks, and finally after 5 years. **Figure 4A** shows that the evolution of the voltammetric profiles upon time is rather small. Interestingly, the reversibility and good definition of the peaks point out that the sample remained clean under these storage conditions. However, arrows indicate changes in the relative peak intensity of the different voltammetric features. As can be seen, the signal associated to hydrogen adsorption on (100) large domains slightly decreases to the detriment of a small increase of the peaks related to hydrogen adsorption on (110) and (100) terrace borders/short domains with increasing conservation time. It is worth noticing that the overall charge under the voltammetric curve remains essentially constant, pointing out the degradation of the (100) terrace sites into the other surface arrangements. Incidentally, it was previously reported that in the presence of oxygen, (100) sites in terraces edges rearrange to form steps of the more energetically favorable (110) orientation [42], which can be considered also as (110) = (111)×(111). These results are in good agreement with the aforementioned beveling of the NCbs edges. Nevertheless, it is important to highlight that even after a long period of storage in the presence of oxygenated species, the electrocatalyst still displays the characteristic response of (100)-preferentially oriented nanoparticles.

On the other hand, carbon monoxide (CO) adsorption and subsequently oxidation (CO stripping) has been traditionally used to bring extra cleanliness to the surface of Pt and Pt-based nanoparticles, and it has also been demonstrated to be a *surface structure sensitive reaction* that can be considered as a surface probe [16, 46]. Thus, small modifications on the surface structure of the nanoparticles originate perceptible modifications on the CO oxidation profile, being peak multiplicity closely associated to the surface site distribution. **Figure 4B** exemplifies this effect: the sharp peak at ca. 0.75 V (characteristic of CO oxidation on {100}-faceted nanoparticles) diminishes, while the preceding shoulder at ca. 0.72 V (associated to CO oxidation on defects present on (100) ordered domains) evolves to a well-defined peak with increasing intensity. The atomic models of **figure 4C** illustrate the surface degradation suggested by cyclic voltammetry. Therefore, despite the simplicity of the experiment, it has been demonstrated that cyclic voltammetry can be used as an invaluable tool to detect subtle changes in the surface structure of the nanoparticles that cannot be easily evaluated by microscopic techniques.

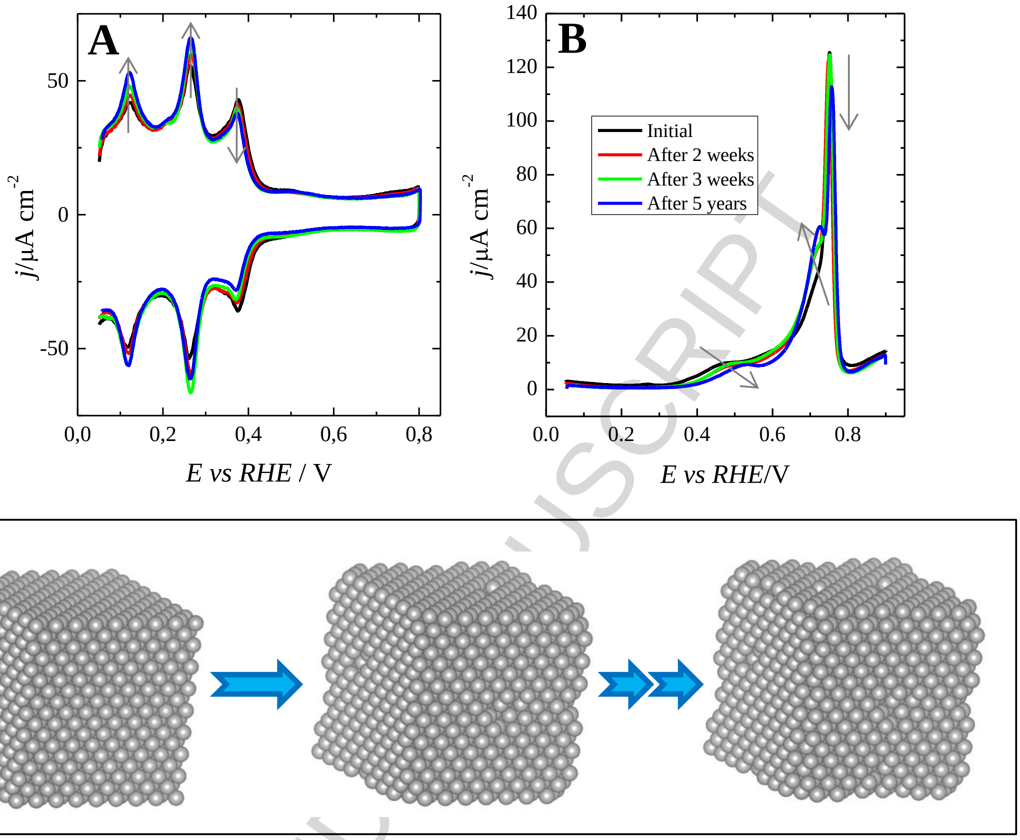

Figure 4. Evolution of the surface structure of a sample of Pt cubic nanoparticles upon time. (A) Cyclic voltammograms and (B) CO strippings were recorded in a 0.5 M H_2SO_4 solution at a sweep rate of 50 mV s^{-1} and 20 mV s^{-1}, respectively. (C) Atomic models for degradation of cubic nanoparticles upon storage time in aqueous solution.

Conclusions

In this work, we offer an abridged overview about *in situ* electrochemical characterization of Pt surfaces, demonstrating its potentiality for the detection of subtle changes in surface structure. The voltammetric profile of (100)-preferentially oriented nanoparticles with high uniformity of shape, prepared by different synthetic methodologies have revealed that comparable responses must be obtained for nanoparticles with similar morphology, independently of the route followed to prepared them. In addition, this paper points out the direct correlation that can be established between simple model surfaces and more complicated nanoparticulated systems. We have shown the particular overlapping of the characteristic fingerprint voltammograms of Pt(510) electrode and Pt NCbs, suggesting the use of this stepped surface to understand the reactivity of (100)-Pt nanoparticles. Structural stability of these cubic nanocatalysts upon long storage time in aqueous solution was examined by observing the changes of the fingerprint peaks that result from surface reordering.

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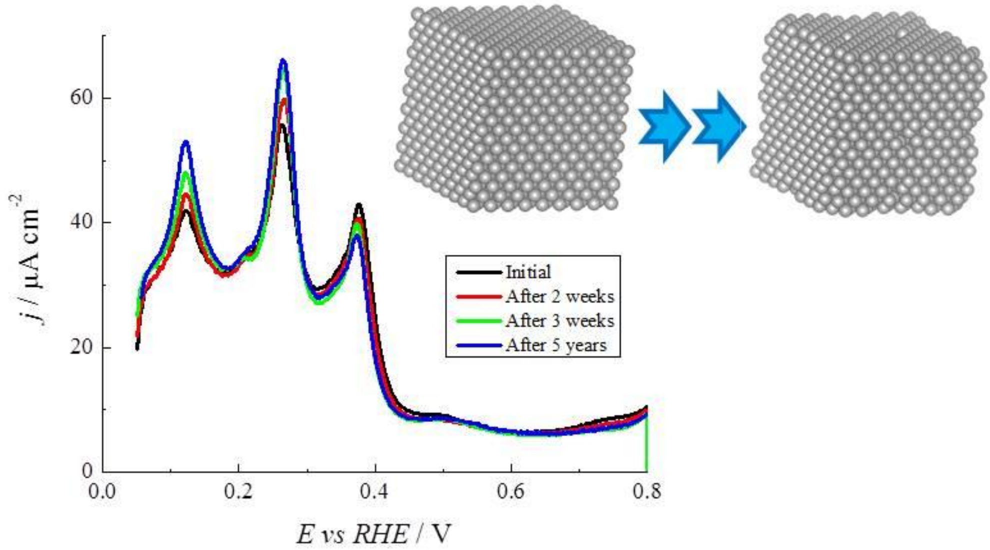

Graphical Abstract

Highlights

“On the quality and stability of preferentially oriented (100) Pt nanoparticles: an electrochemical insight” by, Rosa M. Arán-Ais, José Solla-Gullón, Enrique Herrero and Juan M. Feliu

- Electrochemical characterization of Pt surfaces as potential tool for the detection of subtle changes in surface structure.

- Nanoparticles with similar morphology prepared by different synthetic methodologies must show comparable responses regardless of the route followed to prepare them.

- Direct correlations between simple model surfaces and more complicated nanoparticulated systems can be established.

- Structural stability of cubic nanocatalysts examined by observing the changes of the fingerprint peaks.