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Small (< 5 nm), Clean, and Well-Structured Cubic Pt Nanoparticles: Synthesis and Electrochemical Characterization

R.M. Antoniassi^[a,b], H. Erikson^[a,c], J. Solla-Gullón^[a], R. M. Torresi^[b], J. M. Feliu^[a]

[a] Dr. R. M. Antoniassi, Dr. H. Erikson, Dr. J. Solla-Gullón, and Prof. J. M. Feliu
Instituto de Electroquímica, Universidad de Alicante, Ap. 99, E-03080 Alicante, Spain.
E-mail: aidide@usp.br

[b] Dr. R. M. Antoniassi, and Prof. R. M. Torresi
Depto. Química Fundamental, Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, 05508-000, São Paulo, SP, Brazil

[c] Dr. H. Erikson
Institute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia

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Abstract: Shape-controlled metal nanoparticles are significantly improving the electrocatalysis of many relevant reactions. By controlling the shape of nanoparticles, it is possible to engineer their surface to exhibit a preferential structure. However, to facilitate the incorporation of shaped nanomaterials into practical electrochemical devices, it is indispensable to overcome the limitation due to their large particle size (typically >5 nm). For practical applications, nanoparticles must have size lower than 5 nm with a clean surface to decrease costs and provide a sufficiently large specific surface area. This is a major challenge that has remained unexplored up to now. Herein, we present the synthesis and electrochemical characterization of 3-5 nm but well-defined cubic Pt nanoparticles supported on carbon. The electrochemical characterization of the nanoparticles evidences the existence of a preferential {100} and clean structure (within about 40% of {100} terrace surface).

Most of the relevant electrocatalytic reactions are known to be surface structure-sensitive. Consequently, the use of shape-controlled metal nanoparticles is strongly affecting the electrocatalysis of many important reactions, because it is possible to prepare nanoparticles with a preferential surface by manipulating its structure. Since the first examples of shape-dependent electrocatalysis on cubic-shaped platinum nanoparticles (PtNP) towards ammonia electrooxidation[1], several contributions have been reported in this topic[2]. Despite the significant improvements that shaped metal nanoparticles have achieved for many electrocatalytic reactions, a major drawback relative to the large particle size (>5 nm) is commonly faced for the real implementation of catalysts in practical electrochemical devices[3]. In fact, as stated in some previous contributions[4], getting small (<5 nm, to provide a sufficiently large specific surface area) and shaped metal nanoparticles still remains a challenge due to the unavoidable increase in the percentage of corner and edge surface atoms when the particle reaches this size range.

In this contribution, we report the synthesis and electrochemical characterization of small (3-5 nm) PtNP supported on carbon, having a well-defined cubic shape. The electrochemical characterization of the cubic PtNP clearly points out not only the presence of a highly preferential {100} surface structure but also their surface cleanliness. It is worth recalling that regardless

size[4b], surface cleanliness is a critical parameter for any electrocatalytic process. Most of the shaped metal nanoparticles are prepared by using colloidal routes in which capping agents are employed to engineer the shape of the nanoparticles[5]. Consequently, the shaped nanoparticles must be cleaned to completely remove the surface-regulating agents located at the surface of the nanoparticles[6]. Unfortunately, the surface cleaning is not always achieved, and the catalyst reactivity (activity and/or selectivity) is strongly perturbed by uncontrolled surface contamination.

The one-pot method employed herein is based on the capping-agent-free reshaping of the commercial Pt (quasi-spherical shape)/C(Vulcan) (metal loading: 9 wt%) into preferential cubic PtNP, through a seed-mediated approach by employing bromide ions as shape-directing agent. A detailed description of the experimental procedure is included in the supporting information. The method allows preparing sub-5 nm Pt nanocubes with different metal loadings (25-45 wt%, Tab. S1). Representative TEM images of the samples are found in Fig. 1 and Fig. S1. The starting material displays the presence of well-dispersed 1.6 nm quasi-spherical PtNP (Fig. 1a). Figs. 1b-d show the TEM images of the cubic reshaped PtNP for increasing metal loading. The cubic PtNP are well-dispersed, independently of size or loading. This fact points out that the reduction/deposition of new Pt atoms, essentially occurs onto the existed Pt seeds, which continuously grow and reshape without compromising the particle dispersion. For increasing loadings, 3.1, 4.5 and 4.7 nm nanocubes (Fig. S2) remain below the 5 nm limit. To our knowledge, this is the first report of ultrasmall cubic PtNP displaying simultaneously a preferential and clean surface suitable for electrocatalysis. Some control experiments shown in Figs. S3-S5 demonstrate the importance of both seeds and Br⁻ in the characteristics of the final PtNP structure.

Figure 1. Representative TEM images of a) commercial carbon supported Pt seeds (1.6 nm), and b) 3.1 nm c) 4.5 nm and d) 4.7 nm Pt nanocubes.

The different samples were characterized by XRD, shown in Fig. S6a and Tab. S1. The crystalline sizes are in good agreement with TEM observations. Electronic characteristics of the PtNP were modified through the reshape process. From the XPS results, Fig. S6b and Tab. S2, the commercial 1.6 nm quasi-spherical PtNP displays a high content (about 63%) of oxidized species (Pt^{2+} and Pt^{4+}). Conversely, the Pt nanocubes show an evident preferential metallic state ($< 70\%$).

The proposed reshape method requires the use of large amounts of KBr ($\text{Br}^-:\text{Pt}$ atomic ratios varying from about 275 to 117) because bromide ions are used as shape-directing agent. It is known that Br^- interact with platinum seeds by passivating $\text{Pt}(100)$ sites during the synthesis growth step[7]. However, the amount should be optimized, because a platinum surface covered with such high concentrations of adsorbed bromide would represent an undesirable situation for catalysis, in which the Pt specific active sites would be hampered with the Pt-halogen interaction, thus leading to a decrease in the catalytic activity. To evaluate the amount of bromide adsorbed at the surface of the PtNP, XPS spectra of the Br 3d region (about 193 - 180 eV) was monitored (Fig. S7). Interestingly, low amounts of bromine were detected ($\text{Br}^-:\text{Pt}$ ratio between 0.04 to 0.06, Tab. S2), which points out their effective removal during the cleaning process, as demonstrated by the voltammetric profiles presented herein.

The use of shape-controlled metal nanoparticles to enhance the activity, selectivity and even stability of many relevant electrocatalytic reactions is becoming a routine approach[2]. However, it is important to recall that the shape of the nanoparticles is not the key point controlling the electrocatalytic behavior but their surface structure[2b,8]. Particle shape and surface structure are known to be correlated. However, these correlations are established based on *perfect* polyhedral

nanoparticles, which is a non-realistic situation. Consequently, a reliable tool to characterize the *real* surface details is essential, since the nanoparticle structure can be extremely complex and contains i) domains of various dimensions and different geometries, and ii) a high fraction of surface defects including corner and edge sites. This last point is very relevant for ultrasmall PtNP. In addition, and taken into consideration the intrinsic shape and surface structure heterogeneities of each nanoparticle, the surface structure characterization must give us statistically representative information of the whole sample and not only a few individual nanoparticles because the resulting electrocatalytic activity (for any reaction) will be always the sum of all the specific contributions of each type of surface site present at the surface of each nanoparticle. As discussed in previous contributions[9], some electrochemical probes have demonstrated to be extremely powerful to study the surface structure of different shaped metal nanoparticles. In addition, this characterization is performed with i) a large number of nanoparticles and, consequently, the response is statistically representative of the whole sample, and ii) under similar experimental conditions than those subsequently employed during the electrochemical reactions, that is, the analysis is performed as in-situ. For Pt surfaces, the cyclic voltammetric response in the so-called hydrogen region (involving the hydrogen and anion adsorption-desorption states) obtained in 0.5 M H_2SO_4 , it is widely accepted as the most convenient way to qualitatively characterize their surface structure[9]. The response is used unequivocally as fingerprint of the Pt surface structure and, from the relative intensity of the different signals, it is possible to visualize the existence of any preferential structure.

Figure 2. Voltammetric profiles obtained with a) commercial carbon supported Pt seeds (1.6 nm), and b) 3.1 nm c) 4.5 nm and d) 4.7 nm Pt nanocubes in 0.5 M H_2SO_4 at 50 mV s^{-1} .

Fig. 2 shows the representative voltammetric responses of the materials. Fig. 2a reports the polycrystalline profile (without any preferential surface) of the commercial material. This is expected considering their quasi-spherical shape. The responses obtained with the different Pt nanocubes (Figs. 2b-d) are similar and clearly different to that obtained with the

commercial sample. In all cases, the sharpness and symmetry of the adsorption/desorption peaks evidence the cleanliness of the surface of the Pt nanocubes and confirms that the large amount of bromide employed in the syntheses does not compromise the PtNP surface. Based on previous Pt single crystal studies[9], the peak at 0.125 V corresponds to the hydrogen adsorption/desorption on Pt(110)-type sites, whereas the peak at 0.26 V is due to the Pt(100)-step sites on Pt(111) terraces and also due to those sites close to the steps on the Pt(100) terraces. Much more relevant is the broad contribution observed at 0.35-0.37 V which is known to be attributed Pt(100) bidimensional terraces. Notice that this signal is absent in the voltammogram recorded with the quasi-spherical PtNP. Finally, it is also worth noting a small signal at about 0.55 V which is related to the bi-dimensionally ordered Pt(111) terraces. Interestingly, this voltammetric response is essentially the same than those obtained with larger Pt nanocubes (>5 nm), confirming the preferential {100} surface structure[1,6,8,9]. This preferential {100} surface structure is evidenced by the 0.35-0.37 V contribution, which is due to the existence of well-defined {100} terraces. It is important to mention that the definition and intensity of this signal seems to improve for increasing particle sizes. To properly analyze this fact, it is necessary to study the redox behavior of the spontaneously adsorbed Ge (Fig. S8) from which it is possible to quantify the amount of {100} terraces at any Pt surface[9]. Tab. 1 contains the {100} percentage of ordered domains for all the materials. To complete the analysis, the fraction of {111} obtained by the irreversible adsorption of Bi is also presented. Experimental details of the analyses are included in the Supporting Information.

Table 1. Fraction of {111} and {100} domains determined for different Pt nanoparticles

	1.6 nm Pt nanoparticles	3.1 nm Pt nanocubes	4.5 nm Pt nanocubes	4.7 nm Pt nanocubes
{100} / %	7.7 ± 0.5	38.8 ± 0.5	41.1 ± 0.5	41.4 ± 0.5
{111} / %	7.2 ± 0.5	8.6 ± 0.5	7.6 ± 0.5	7.1 ± 0.5

Results in Tab. 1 corroborate to the voltammetric profiles. As expected, the commercial Pt nanoparticles contain a poor fraction of well-ordered {111} and {100}. Contrary, the Pt nanocubes have about 40% of active {100} domains, which is remarkable close to the maximum theoretic value of 45% for a perfect 3 nm cube[10]. Besides, these {100} values are comparable with those previously obtained with larger Pt nanocubes, which points out the quality of the present samples despite their small particle size.

Despite ammonia oxidation has been widely used as a sensitive reaction for unsupported Pt(100) nanoparticles, this choice is inconvenient for supported materials with different loadings, because it is highly affected by the deposit thickness on the electrode[12c]. Instead, formic acid (FA) electrooxidation is considered simultaneously as a viable alternative to the H₂-fed fuel cells and a model reaction to study structural surface details of Pt single crystals[11] and PtNP[12]. As expected, the reshaped materials respond rather similar, independently of the size. The negative scan of the voltammetry profile of the Fig. S9

and Fig. S11 show a typical two waves peak-shoulder-like curve for the Pt nanocubes. This profile was also observed with larger cubic PtNP[12]. Specifically, the peak at 0.47 V is attributed to the FA oxidation onto Pt(100) facets, while the shoulder at about 0.73 V comes from to the process on other Pt sites. The signal at 0.43 V is dominant, which reflects the preferred {100} surfaces of the synthesized materials. Pt(100) is known to be the most active surface for FA, but also the most sensitive to CO-poisoning[12c]. In the positive scan, the activity is very low as a consequence of the CO poisoning but, in the negative scan, the activity significantly increases due to the high fraction of {100} surface domains. The Pt nanocubes containing about 41% of {100} terraces display the highest current density, which is more than 50 % superior than that obtained with the 1.6 nm quasi-spherical Pt nanoparticles (about 3.6 and 2.3 mA cm⁻², respectively). However, the activity of the 3.1 nm Pt nanocubes (having about 38% of {100} terraces) is about 2.9 mA cm⁻² which is only 26% superior than the commercial ones and much lower than that obtained with the Pt nanocubes having only a 3% more of {100} terraces. This suggests that the total percentage of {100} is not the only parameter affecting the resulting activity and that particle size and/or metal loading and/or the size of the {100} domains may also play a role in the activity in the positive going sweep during the electrooxidation of FA. At this respect, for instance, it is known that by decreasing the particles size, the CO poisoning is importantly reduced due to the lack of a Pt site ensemble for the CO poisoning process[13]. This is clearly observed in Fig. S10, where the 1.6 nm quasi-spherical Pt nanoparticles display a high activity in the positive going sweep in comparison with the Pt nanocubes. More work is in progress to understand this finding.

Figure 3. Maximum current densities obtained in 0.5 M HCOOH + 0.5 M H₂SO₄ at 20 mV s⁻¹ with the different Pt nanoparticles.

In summary, sub-5 nm carbon supported Pt nanocubes have been prepared through a simple reshaping methodology. Their electrochemical characterization indicates that the Pt nanocubes are clean and display a preferential {100} surface structure with about 40% of {100} terraces. This finding represents a major advance in this topic and may strongly contribute to the future implementation of shaped metal nanoparticles into practical electrochemical devices.

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Keywords: Electrochemistry • nanoparticles • particle shape • particle size • surface structure

- [1] F. J. Vidal-Iglesias, J. Solla-Gullón, P. Rodríguez, E. Herrero, V. Montiel, J. M. Feliu, A. Aldaz, *Electrochem. Commun.* **2004**, *6*, 1080-1084.
- [2] a) W. Hong, Y. Kim, Y. Kwon, S. W. Han, *Chem. Asian J.* **2016**, *11*, 2224-2239; b) P. Strasser, M. Gliech, S. Kuehl, T. Moeller, *Chem. Soc. Rev.* **2018**, *47*, 715-735; c) R. Rizo, B. Roldan Cuenya, *ACS Energy Lett.* **2019**, *4*, 1484-1495.
- [3] a) C. Wang, H. Daimon, Y. Lee, J. Kim, S. Sun, *J. Am. Chem. Soc.* **2007**, *129*, 6974-6975; b) T. Yu, D. Y. Kim, H. Zhang, Y. Xia, *Angew. Chem. Int. Ed.* **2011**, *50*, 2773-2777; c) J. Solla-Gullón, F. J. Vidal-Iglesias, J. M. Feliu, *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **2011**, *107*, 263-297; d) H. You, S. Yang, B. Ding, H. Yang, *Chem. Soc. Rev.* **2013**, *42*, 2880-2904; e) S. E. F. Kleijn, S. C. S. Lai, M. T. M. Koper, P. R. Unwin, *Angew. Chem. Int. Ed.* **2014**, *53*, 3558-3586; f) L. García-Cruz, V. Montiel, J. Solla-Gullón, *Phys. Sci. Rev.* **2019**, *4*, 2017-0124.
- [4] M. Zhao, X. Wang, X. Yang, K. D. Gilroy, D. Qin, Y. Xia, *Adv. Mater.* **2018**, *30*, 1801956; b) K. Miyabayashi, S. Nakamura, M. Miyake, *Crys. Growth and Design* **2011**, *11*, 4292-4295.
- [5] a) Y. Xia, X. Xia, H.-C. Peng, *J. Am. Chem. Soc.* **2015**, *137*, 7947-7966; b) T.-H. Yang, Y. Shi, A. Janssen, Y. Xia, *Angew. Chem. Int. Ed.* **2020**, *59*, 15378-15401.
- [6] M. A. Montiel, F. J. Vidal-Iglesias, V. Montiel, J. Solla-Gullón, *Curr. Opin. Electrochem.* **2017**, *1*, 34-39.
- [7] a) Y. Xia, Y. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem. Int. Ed.* **2009**, *48*, 60-103; b) N. Ortiz, S. E. Skrabalak, *Langmuir* **2014**, *30*, 6649-6659.
- [8] F. J. Vidal-Iglesias, J. Solla-Gullón, E. Herrero, V. Montiel, A. Aldaz, J. M. Feliu, *Electrochem. Commun.* **2011**, *13*, 502-505.
- [9] a) J. Solla-Gullón, P. Rodríguez, E. Herrero, A. Aldaz, J. M. Feliu, *Phys. Chem. Chem. Phys.* **2008**, *10*, 1359-1373; b) J. Solla-Gullón, J. M. Feliu, *Curr. Opin. Electrochem.* **2020**, *22*, 65-71.
- [10] S. Liu, C. Sun, J. Xiao, J. L. Luo, *ACS Catal.* **2020**, *10*, 3158-3163.
- [11] V. Grozovski, V. Climent, E. Herrero, J. M. Feliu, *Phys. Chem. Chem. Phys.* **2010**, *12*, 8822-8831.
- [12] a) J. Solla-Gullón, F. J. Vidal-Iglesias, A. Lopez-Cudero, E. Garnier, J. M. Feliu, A. Aldaz, *Phys. Chem. Chem. Phys.* **2008**, *10*, 3689-3698; b) M. N. Krstajić-Pajić, S. I. Stevanović, V. V. Radmilović, A. Gavrilović-Wohlmuther, V. R. Radmilović, S. Lj. Gojković, V. M. Jovanović, *Appl. Catal. B* **2016**, *196*, 174-184; c) F. J. Vidal-Iglesias, V. Montiel, J. Solla-Gullón, *J. Solid State Electrochem.* **2016**, *20*, 1107-1118.
- [13] S. Park, Y. Xie, M. J. Weaver, *Langmuir* **2002**, *18*, 5792-5798.

Entry for the Table of Contents

Synthesizing small (< 5 nm), clean and shaped metal nanoparticles would strongly contribute in the search of better electrocatalysts. Herein, we report the preparation and electrochemical characterization of Pt nanocubes fulfilling all these requirements, that is, a particle size smaller than 5 nm, and a clean and preferential {100} surface structure (~ 40% of {100} terraces). This finding represents a significant advance in electrocatalysis.