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A new methodology for quantifying the surface crystallography of particles from their tomographic reconstruction: application to Pd nanoparticles embedded in a mesoporous silica shell

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Abstract

In this work, we propose an experimental approach allowing for the identification and the subsequent quantification of nanoparticles crystallographic facets, based on 3D data obtained using Transmission Electron Microscopy (TEM). The particle shape and faceting can be determined using Electron Tomography (ET) combined with High-Resolution TEM (HR-TEM). The quantitative analysis of faceting is carried out on the particles 3D model using a geometrical approach that automatically detects planar regions on particle boundaries. In order to check the reliability of our approach, we analysed palladium particles confined inside or located at the outer surface of a mesoporous silica shell (Pd@SiO₂) after an annealing treatment at 250°C under H₂ for 12 h. From the materials perspective, the aim of the current work is to investigate the encapsulation effect of silica (SiO₂) shells on the change in morphology and faceting of palladium NPs during such annealing treatment.

Introduction

In the recent development of nanoscience, the nanoparticles (NPs) surface faceting is a key parameter allowing modulating and optimising the properties of metal/oxide NPs in several applications, especially in catalysis. The case of palladium (Pd) has been extensively studied due to its facets depending catalytic behaviour^{1,2,3,4,5} and it was demonstrated, for instance, that such faceting has profound implications on its activity in hydrogenation dynamics.⁶ As a catalyst for acetylene hydrogenation, experimental and theoretical results revealed that Pd (100) facets do exhibit higher conversion and better ethylene selectivity than Pd (111) facets.^{7,8,9,10} Also, recent papers reported such a faceting-dependent effect namely higher catalytic performances of Pd nanocrystals enclosed by (100) facets compared to those enclosed by (111) facets for formic acid oxidation and furan hydrogenation reactions.^{11,12} Otherwise, (111) faceted palladium was found to display a higher activity than (100) faceted one in selective alkyne hydrogenation.¹

Also, palladium as a catalyst is known to suffer sintering and diffusion at high temperature when deposited on classical supports such as alumina. In order to improve its thermal stability and to prevent the sintering effect, new palladium based catalysts such as core-shell Pd@mesoporous SiO₂ nanostructures were developed. The as-confined palladium was reported to ensure a better activity and in particular a higher stability before deactivation than the classical Pd/SiO₂.^{13,14,15} The control of the shape/faceting of the palladium core in such Pd@SiO₂ nanostructures was reported by several groups. Martins *et al.* succeeded in synthesizing Pd@SiO₂ with controlled morphologies of the Pd cores having cubic, octahedral or icosahedral shapes for application in CO₂ hydrogenation.^{16,17}

Despite the great benefits of controlling NPs faceting, quantitative analysis of the surface crystallography and, in particular, of the individual contributions of the various facets present at the external surface of catalytic NPs is still technically very challenging, however, this requirement becomes nowadays essential towards design and control of the catalyst structure and performance. Significant efforts have been devoted to quantify the NPs shape and faceting mostly from two-dimensional (2D) imaging techniques obtained generally from the axis length distribution using specific algorithms or modelling based on crystallographic considerations.^{18,19,20,21,22,23} The tomographic techniques especially the electron tomography (ET) remain the most appropriate ones for ensuring the access to such 3D information on particles with an external shape far from that of ideal platonic solids.^{24,25,26} In order to properly quantify their surface faceting one needs to address the following points: (1) to accurately identify the 3D general shape and the facets present at the particle surface and (2) to perform automatic recognition to be applied to a large number of particles allowing a significant statistical analysis. Several papers reported the analysis of particles faceting from tomographic data, but most of them used approaches, which considered a “template” shape but not the real geometry of the crystal.^{27,28} Other proposed procedures are able to recognize the basic shape, but not the size of each crystal face,^{21,29} and/or were validated only on simulated data.^{30,31} Kovačević *et al.* reported the identification of the faceted crystal shape from a microcomputed tomography (μ CT) analysis using a 3D Hough transform and a parametrized representation of the shape.³¹ Several other 3D studies published in the last decade have used the electron tomography for solving the faceting of crystalline nanoparticles. In one of them, the external crystallographic facets have been determined by using the direct proportionality between the intensity of the high angle annular dark field (HAADF) images and the thickness in the particular case of homogenous particles;³² this approach is limited to the use of HAADF mode for the tilt series acquisition and consequently to the study of particles made of heavy elements that provide a good enough signal to noise ratio in such images. Other similar reported studies are based on a direct comparison between the external surface of the 3D model and the equilibrium shapes of the most

common crystals;³³ this qualitative approach is, once again, particularly appropriate for the study of some basic external shapes, with well-defined truncations, and requires an individual analysis of each particle, at various locations on its external surface, which is a very time-consuming protocol. To the knowledge of the authors, the most significant work on the 3D quantification of crystals facets was reported by Grothausmann *et al.* on the automated quantitative 3D analysis of datasets obtained using focus ion beam (FIB) tomography via an algorithm allowing the analysis of the probability distributions of the orientations of triangles normal in mesh representations of the crystals.³⁴ In the quasi-absence of automated approaches for facets quantification, the most common evaluation of facets and/or interplanar angles are manually determined,^{34,35} which is a difficult and time consuming task prone to errors, especially if several particles, different in terms of the relative amounts of the external facets, are present in the analysed sample.

Herein, we do investigate the 3D shape and faceting of palladium NPs in Pd@SiO₂ nanostructures after a thermal reduction treatment under H₂ at 250°C for 12 h and the possible effect on their thermal evolution due to the encapsulation with silica shells by comparing NPs localized (1) inside and (2) at the outer surface of the silica. For this purpose, we use a new 3D geometrical approach of automated facets quantification based on surface normal analysis applied on 3D data deduced from electron tomography (ET) experiments. To put crystallographic information into the 3D morphology of nanoparticles, several high-resolution TEM (HR-TEM) images were acquired during the ET experiment at tilt angles for which the nanoparticle orientations correspond to high symmetry zone axes with respect to their crystal lattice. From a methodological point of view, our aim was to develop an easy-to-apply protocol for the quantitative analysis of the surface facets of the nanoparticles from 3D models obtained using “classical” electron tomography, which is not a routine method, but it can however be applied on several particles in the same experiment and that with a resolution less than a nanometer.

Results and discussion

The samples

Figure 1A-B presents TEM images of typical Pd@SiO₂ nanostructures after the thermal treatment i.e. reduction under H₂ at 250°C for 12 h (several supplementary images are shown in Figure 1-SI). As reported in a previous work, the images do show that the palladium cores do display a mixture of icosahedral and polyhedral shapes with a relatively narrow size distribution around a size of 17±3 nm.^{16,36} The silica shell is about ~70 nm thick and exhibits a mesoporous character characterized by pores with a radial orientation from the Pd core to the external surface of the shell (Figure 1B). It is worth noting that, in our specimen, almost all the palladium nanoparticles are localized inside a silica shell, only a few ones are observed at the external surface of the shell (highlighted by red squares). The presence of these two shapes of palladium particles was already observed for the synthesized NPs before their encapsulation by the silica shell (Figure 2-SI) and it was reported that such inhomogeneity of the morphologies could result from different growth kinetics due to the use of CTAB as capping agent during the synthesis.^{37,38}

Figure 1. A-B) TEM images and C) STEM ADF image (in inset, the corresponding STEM BF image) of typical Pd@SiO₂ nanostructures consisting in Pd particles inside and at the external surface of the silica grains; D) STEM EDX maps of Si, O and Pd elements carried out on the Pd@SiO₂ shown on the image C. Oxygen map show the presence of O traces in the external Pd particles (white squares).

The particles at the external surface of the silica aggregate were found to have a larger size and a slightly different morphology (Figure 2-SI). At this stage, similar 2D “apparent” shapes can be also observed for some encapsulated particles when observed from different angles. In order to investigate precisely the difference in morphology between the two types of palladium particles we studied their 3D shape using Electron Tomography. It is worth noting that the probably different morphologies and/or sizes of the palladium particles at the outer silica surface most probably result from the annealing treatment at 250 °C, as these particles were not confined in a silica shell and were then more exposed to the effect of temperature and gas pressure. Distribution of the palladium and silicon elements within the nanostructures was measured on typical Pd@SiO₂ particles presenting palladium inside and outside of silica using energy-dispersive X-ray spectroscopy (EDX) (Figure 1C-D). The Pd and Si maps are consistent with the expected core-shell structures and do confirm that both particles are made of palladium. Moreover, the EDX analysis shows that the external palladium particles are oxidized (see oxygen map), this information could not be verified in the case of the internal palladium due to presence of oxygen from the silica shell.

At first, electron tomography experiments were carried out on two typical palladium particles encapsulated in silica, with both octahedral and icosahedral shapes, respectively (Figure 2A). The obtained 3D models allow confirming that the studied octahedral-like particle displays several well identified facets with relative orientations in agreement with those of the eight facets in a regular octahedron. For the icosahedral particle, twenty (20) facets are expected, in agreement with an icosahedral shape. The HR-TEM images of representative palladium cores do show that the two types of particles are well crystallized, however the octahedral particles display monocrystalline structure (Figure 2B) while the icosahedral ones do exhibit a multi-twinned structure (MTPs) (Figure 2C).

Figure 2. (Columns from left to right): (A) STEM BF image (in inset the corresponding STEM ADF image) and 3D model of two typical Pd@SiO₂ with inside an octahedral and an icosahedral Pd particles. HR-TEM image, with zooms on the highlighted zones, the corresponding FFT micrograph and 3D models of typical (B) octahedral and (C) icosahedral core palladium.

The spots on the FFT (Fast Fourier Transform) micrographs obtained from the HR-TEM images of the two particles were easily indexed to the reflections of the fcc lattice of metallic palladium (Card JCPDS n° 05-0681): the measured d_{hkl} distances of 0.12 nm, 0.19 nm and 0.22 nm do correspond to the planes (220), (100) and (111), respectively. An additional distance of 0.34 nm was measured for the icosahedral particle, which could be the result of a moiré pattern due to overlapping crystallites as usually reported in the literature.³⁹

Quantifying the facets

In order to quantify the 3D faceting of the palladium nanoparticles, the external surface of each 3D model was split into corresponding facets with a geometrical approach using surface normal analysis. To do this, each nanoparticle volume is converted to a 3D surface, with normals computed for each vertex. We can then automatically assign vertices to flat regions and non-flat regions. Flat regions are defined as groups of vertices with similar normals, while non-flat regions are defined as vertices for which the normal deviates from planar regions by more than 20°. Non-flat regions are mostly located on edges between facets (for more details, see the Experimental Methods section and Figure 3SI). We should mention that, with respect to the previously reported methodologies for the quantification of the particle faceting, the data analysis protocol we propose can be automatically applied to all the particles from the reconstructed volume, without any specific adjustment from a particle to the next one. In addition, the present protocol is not restricted to the identification of the facets as it the case of some of the previous reported studies, but it also allows for a quantification of the facets areas by using the 3D representation obtained through tomography. Finally, because in the treatment only the spatial coordinates of the surface voxels are considered, it is not sensitive to the intensity distribution inside the 3D reconstruction for which the use of an incoherent mode (such as the HAADF one) is mandatory.

Figure 3. Protocol of 3D facet identification via HR-TEM and ET realized on (up) octahedral Pd particle at 41° and 7° and (bottom) icosahedral MTP at -10° and 30° on different regions of the particle. A) and B): high resolution TEM images, corresponding FFT micrographs and 3D surface models, with the identified facets in different colours, for the octahedral particle. C) and D) A) and B): high resolution TEM images, corresponding FFT micrographs, 3D surface models, with the identified facets in different colours, for the icosahedral particle; the 3D representations of an ideal icosahedron, using similar angular orientations, are also depicted; in C), four local high resolution images corresponding to the particles areas schematized on the global image and associated FFT micrographs, are also shown.

The crystallographic facets were identified using the HR-TEM-HR images taken during the ET experiment when the particle orientation corresponds to a zone axis of the crystal; that allows for a proper 3D identification and a subsequent quantification of the crystallographic facets that are parallel to the considered zone axis, as well as their spatial distribution at the particle surface. Figure 3 illustrates a typical 3D identification and quantification of the present facets from the 3D reconstructed model of palladium particles visualized at angles of 41° and 7° in the case of octahedral particle and of -10° and 30° in the case of icosahedral-like particle. Note that the values of tilt angles are given from the initial position (0°) of the particle on the TEM grid, and do correspond to the angles when the particle is well oriented along a zone axis with respect to the electron beam. Additional views along other typical angles are present in Figure 4-SI and 5-SI.

Using the geometrical approach of facets quantification, the octahedral particle was found to exhibit four (111) facets, two (100) facets and one (220) facet, presenting 61.2%, 18.9% and 5.3% of the total particle surface, respectively (Table 1SI). The surface not classified as facet (for which the voxel

normals are well different from the mean orientations of the main facets) presents 14.5% and is mostly located around the edges of the particle facets.

The case of the icosahedral MTP is found to be more complex due to the “polycrystalline” structure of the particles, which inhibits the direct identification of crystallographic facets using the HR-TEM images. A first visual analysis of the 2D TEM images extracted from the tilt series shows that, at some specific angular positions, the symmetry of the 2D shape of the particle is very close to the one of an ideal icosahedron (Figures 3C, 3D and 5SI). As a consequence, we can consider that all the twenty facets assigned to an icosahedral shape are well present at the surface of the particle. We set this number of allowed facets in our data treatment approach, that corresponds to fitting the external surface of the 3D model with twenty well-defined planar surfaces. The angular positions of the as-obtained surfaces correspond to the relative orientations of the twenty facets in an icosahedron. As a result, they can be assigned to the twenty (111)-type planes which generally surround a MTP particle. This is in very good agreement with the orientations of the associated “twinned” adjacent crystals deduced from the high resolution 2D images (Figure 3C). A very important finding arises from the quantitative analysis of the surface areas of these twenty (111) facets we deduced by using this protocol (the corresponding values are summarized in Table 2SI). We can observe they do not cover all the surface of the particle, but only about 78%, which is in fact the estimated relative contribution of the (111) facets to the total surface. The remaining part cannot be explicitly assigned to other types of facets, for two main reasons: the first one, is that it is difficult to properly define a facet at the interface between two different crystals adjacent in the icosahedral structure, and the second one, is that our 3D resolution doesn’t allow for unambiguously solve the likely presence of some minor facets which, as the 2D images suggest, are quite small and poorly defined. As a consequence, this data analysis geometrical approach applied to icosahedral-like particles allows us principally to separate their global surface into two parts: 22% for which the corresponding voxels cannot be reasonably assigned to a well-defined crystallographic surface and 78%, the contribution of (111) facets, which is well dominant, in agreement with other studies reported in the literature.^{16,40}

The theoretical relative amounts of (100) and (111) facets in ideal octahedrons, icosahedrons and truncated octahedrons are also given for comparison in Table 1. The octahedral palladium particle studied here were found to present a mixture of (100) and (111) facets differing from the perfect octahedron shape. As mentioned, the icosahedral particle present 78% of (111) facets similarly to an ideal truncated octahedron, but the polycrystalline structure, the orientations of the different crystals inside the particle, its external symmetry, as well as the number, the relative orientation and the geometrical shape of the well-defined facets allowed us to unambiguously assigned an icosahedral-like shape to these MTP particles.

The results of the different crystallographic facets quantification for the octahedral and the icosahedral palladium particles obtained in the present work are given in the Table 1, in comparison with the results obtained previously by DRIFT (Diffuse Reflectance Infrared Fourier Transform) measurements applied on the same sample of Pd@SiO₂ nanostructures.¹⁶ In this previous work, the quantification of (100) facets yields a percentage of 39%.¹⁶ It is worth noting that the DRIFT technique is based on the total multi-bonded CO adsorbed and provides only the global amount of the (100) facets, averaged on both type of particles (it does not take into account the shape of the particles). It is also important to mention that the signal assigned to (100) facets in DRIFT can also include contributions from edges and steps that are not possible to quantify using our protocols.^{41,42} From such an analysis, by considering that the (100) and (111) crystallographic planes are the dominant facets at the surface of the particle, we can deduce, by difference, the contribution of the (111) facets to the total surface, which

is about 61%. Given that our protocol allows to measure analogously, for the two types of particles, this (111) contribution, we can use this parameter for a direct comparison between the two types of results. On this regard, by considering that the particle surface mainly contains (111) dominant facets for both types of particles: i) for the octahedral one, the contributions of (111) facets deduced by 3D-TEM and DRIFT are very similar (about 61%); the 39% difference is assigned by DRIFT to (100) facets and to defects in terms of edges and steps, while for the 3D-TEM it corresponds to (100) and (110) facets; ii) for the icosahedral one, the contribution of the (111) facets deduced by our 3D approach is larger (78%) than the 61% value deduced from DRIFT. Two hypothesis may be used for explaining this difference: i) the twenty (111) facets of the icosahedral-like particles do contain lots of local defects (steps for instance) that the DRIFT analysis finally assign to (100) planes; ii) the small relative proportion of the icosahedral-like particles as compared to the octahedral particles (for which the comparison 3D-TEM vs DRIFT is in good agreement). As a consequence, we can consider that, globally, our results are in a good concordance with those obtained by DRIFT. However, the present TEM-based approach gives additional information about the real morphology of particles, since we can identify typical (220) facets (for the octahedral particles) and edges and defects which don't give a separate contribution in DRIFT. Also, we are able to selectively quantify the relative amount of the present crystallographic facets individually for each particle.

Table 1. Proportions of (100), (110) and (111) facets of the octahedral and icosahedral particles determined experimentally by TEM (our approach) and by DRIFT on the same sample (from the [ref 16](#)) in comparison with the theoretical proportions in regular octahedron, icosahedron and truncated octahedron.

43	Relative amounts of facets deduced from experiments			Relative amounts of the facets in ideal crystals		
	TEM		DRIFT ¹⁶	Octahedron	Icosahedron	Truncated octahedron

	octahedron	icosahedron				
(111) (%)	61.2	77.6	61	100 %	100 %	77.6 %
(100) (%)	18.9	-	39			22.4 %
(220) (%)	5.3					
Not identified	14.5	22.4				

From a phenomenological point of view, we investigated previously the dynamical thermal evolution of these palladium particles under conditions similar to the ones used in the present annealing treatment (under H₂) and we found that the particle faceting is stable up to 300°C.³⁶ In the current work, we can consider that the quantified faceting of the two types of particles does not change dramatically during the reduction step due to the presence of the silica shell, which inhibits the palladium diffusion and/or sintering.

In order to directly investigate the effect of the encapsulation by silica on the morphological evolution of the nanoparticles during an annealing step, we have comparatively studied the changes in size and in morphology/faceting of the few palladium particles located outside a silica shell ([Figure 4](#)).

Figure 4. A) STEM-BF image of a typical Palladium particle localized in the outer surface of a silica shell, B) Tilted STEM-ADF images of the particle highlighted in A). 3D faceted models of the particle highlighted in A) at different angles of observation C) before and D) after the quantification approach.

First, we can observe that these particles do present a larger size (30-40 nm) and a less faceted structure (octahedral shape) with well-rounded corners. In addition, compared to the palladium particles located inside the silica shells, the “outer” particles do appear less dense and more “transparent” to electrons despite their larger size, which can reveal less mass contrast when the particles are observed by TEM (Figure 4A and Figure 2SI). Such an aspect has not been observed before the thermal treatment and does certainly result from a different effect of the reduction step for the nanoparticles which are not confined inside the silica medium. Indeed, the palladium is known to easily diffuse under H_2 at high temperature.^{44,45} The size increase of the external particles could be the result of diffusion and sintering mechanisms of residual Pd precursors present in the silica pores or from the other not confined particles during the thermal treatment. From a morphological point of view, the general shape of the particles characterized by the presence of rounded facets at the end of the reduction step was also reported in the case of other platinum particles under H_2 and was explained by the adsorption of the H_2 molecules at the palladium surface, which decreases the free energy of the facets.⁴⁶

In the same way, we tried to identify the crystalline structure of these particles using HR-TEM during the ET experiment, but unexpectedly no diffraction micrographs could be obtained. This can be probably explained by an amorphization and/or by the presence of an important disorder of the palladium during the thermal treatment under hydrogen. Indeed, several groups reported such an amorphization behaviour of nanometric palladium particles due to their interaction with hydrogen.^{47,48} The H_2 molecules do dissociate at the palladium surface and atomic hydrogen H can diffuse into the lattice to form hydrides (PdH_x).⁴⁸ Such diffusion from the surface leads to the formation of an amorphous layer replacing the metallic atoms initially present and ordered on a crystalline lattice.^{47,48} In our case, the reduction treatment was significantly long (around 12 hours), which can induce the formation of a thick amorphous layer leading to the full amorphization of the palladium particle due its

nanometric size. Note that the insider particles are very probably “protected” against these effects thanks to the silica shell.

Despite the absence of an evident crystalline structure for the palladium particles non confined in silica, such a representative Pd-based particle was characterized using electron tomography (particle highlighted by a red square in [Figure 4](#)) in order to quantify its morphological evolution using an approach similar to the one used for the confined particles. As a result, the particle was found to display a regular octahedral shape with eight (08) triangular facets originating from the initial ones; supposing that the amorphization process is topotactic, the facets originate from the initial (111) ones as usually reported in the literature for the metal (Pd) having octahedral morphology.^{49,50,51} The automated facets identification protocol suggests the presence of three (03) additional «minor facets» localized at the facets edges between the principal ones ([Figure 4](#)), which can be explained by the fact that the particle undergoes a restructuring process involving a shape evolution towards a spherical shape due to a surface energy decrease induced by the interaction with hydrogen during the thermal treatment. From a quantitative point of view, the quantification reveals the presence of 77.6% of the total external particle surface as principal facets, 13.5% as minor facets and 8.8% as not identified surface corresponding to non-flat areas ([Table 3SI](#)).

Finally, from a methodological point of view, it is also important to mention that the surface crystallography of the experimental particles was determined here with a sub-nanometer resolution but not with an atomic one. As a consequence, facets with a small surface size (defined only by a small number of voxels) or isolated voxels with the associated normal axes significantly deviated with respect to the axes of the neighbors, cannot be considered in the analysis. As a consequence, the identification of small islands or holes in the surface is thus not performed. Another important point regarding the potential use of this protocol to the study of other crystalline nanoparticles, this quantitative approach is suitable for particles with a mean size ranging from a tenth of a nanometer to about 50 nm. For particles smaller than 10 nm, the facets are not well defined, especially the minor ones, and in this case the use of this approach is not appropriate or not necessary. For particles with sizes higher than 50 nm, the major facets could be yet identified given their spatial extension and possibly directly deduced from their general views obtained using classical 2D TEM; however, for such particles, the resolution which can be reached in the 3D mode is not high enough to be able to identify the minor facets and their spatial delimitation with respect to the major ones.

Conclusions

Herein, we report on a new quantitative 3D approach, which allows for the identification and the quantification of crystallographic facets of particles from their 3D models obtained by Electron Tomography. The as-developed approach was here successfully applied to investigate the faceting of the palladium particles in Pd@SiO₂ core-shell systems, and could be extended to several other nanomaterials or nanostructures presenting facets at the surface, in particular to other metal/oxide nanoparticles. In addition, in our case, the faceting of the palladium particles shelled or at the outer surface of the silica medium was investigated in order to study the effect of the encapsulation of the latter during a thermal treatment under H₂ at 250°C.

Two types of core palladium particles were found and display icosahedral and octahedral shapes with twelve and seven facets, respectively. The quantification approach applied on typical palladium particles allows quantifying the relative amount of (111) facets for both types of particles and also that of minor (100) and (220) facets for the octahedral ones. In the absence of the encapsulation by silica, the particles located at the silica surface do display a larger size and an amorphous layer due to

its interaction with H₂ during the thermal treatment. The electron tomography performed on a typical “external” palladium particle shows a regular octahedral morphology with 8 principal triangular facets and 3 minor facets located at the edges. As a final point, we mention that in this reported work, the two selected particles (with octahedral and icosahedral shapes) have been considered as representative of the all core palladium particles located inside the silica shell. However, it is obvious that the obtained facets quantification needs to be applied on several particles in order to obtain a statistical evaluation representative of the sample, which is now possible using such an automated quantitative procedure for the analysis of 3D nanoscale reconstructions. This approach could be generalized and specifically used for the data analysis of high resolution tomograms, in relation with the development of atomic resolution electron tomography which is achievable nowadays by combining the acquisition of high-resolution tilt series and reconstruction methods in the Fourier space

Experimental methods

Pd@SiO₂ preparation

The Pd@SiO₂ nanostructures were synthesized following the procedure detailed in ref **16** which consists in three steps: (1) a seed mediated growth of Pd particles from isotropic colloids of 3-4 nm following the Nikoobakht method,⁵² (2) the Pd encapsulation by a mesoporous silica shell and (3) the thermal treatment at 250 °C under H₂.

Palladium NPs synthesis via a seed mediated growth method: 180 ml of a K₂PdCl₄ (2.7mM) solution was added to 150 ml of a hexadecyltrimethylammonium bromide (CTAB) 95 mM under stirring at 30 °C under H₂ atmosphere. Then, 6 ml of a sodium ascorbate 80 mM were added and the final solution was stirred at 30 °C for 4 h under H₂.

Silica shell growth: 300 ml of H₂O, 260 ml of EtOH and 3.5 ml of NH₄OH 28wt.% aqueous solution were added to the previous colloidal solution of nanoparticles.

In order to obtain core@shell Pd nanoparticles with a mesoporous silica shell (Pd@m-SiO₂), 1 g of tetraethylorthosilicate (TEOS) is added afterwards drop wise under strong magnetic stirring and the mixture is left to maturation overnight under moderate stirring at room temperature.

After maturation and EtOH addition, the suspension was centrifuged (20 min, 14,000 rpm) to recover the precipitate.

Reduction treatment: The black solid is then dried under air at room temperature and finally treated in hydrogen flow at 250 °C for 12 h (heating rate of 2 °C min⁻¹).

Transmission Electron Microscopy (TEM) and Scanning TEM (STEM)

The samples were dispersed in ethanol and deposited on a holey carbon coated TEM grid. Transmission electron microscopy (TEM) analysis was carried out using a JEOL 2100 FEG S/TEM microscope operated at 200 kV equipped with a spherical aberration corrector on the probe forming lens. For scanning transmission electron microscopy (STEM) high-angular annular dark field (HAADF) analysis, we used a spot size of 0.13 nm, a current density of 140 pA, a camera focal length of 8 cm, corresponding to inner and outer diameters of the annular detector of about 73 and 194 mrad.

Energy-dispersive X-ray spectroscopy (EDX)

Elemental analyses were carried out in STEM mode with an energy dispersive X-ray spectroscopy (EDX) probe using a silicon drift detector (SDD) with a sensor size of 60 mm².

Electron Tomography

The acquisition of tilt series was performed using the tomography plug-in of the Digital Micrograph software, which controls the specimen tilt step by step, the defocusing and the specimen drift. The HAADF and BF tilt series in the STEM were acquired simultaneously by using the ADF and BF detectors

and tilting the specimen in the angular range of $\pm 76^\circ$ using an increment of 2° in the equal mode, giving thus a total of 77 images in each series. The recorded images were spatially aligned by cross correlating consecutive images using IMOD software.⁵³ For the volume calculation, we used the algebraic reconstruction technique (ART)⁵⁴ implemented in the TomoJ plugin⁵⁵ working in the ImageJ software.⁵⁶ Finally, the visualization and the analysis of the final volumes were carried out using the displaying capabilities and the isosurface rendering method in the Slicer software.⁵⁷

As usual in electron tomography studies, a very important concern is the estimation of the 3D resolution and the influence of the tomographic artefacts on the relevance of the reconstruction. At this regard, by considering the total number of recorded projections, the mean size of the analyzed objects and the analytical relations given in ref.⁵⁸, the resolution of the tomograms was estimated to be about 0.5 nm in the direction perpendicular to the electron beam axis and to the tilt axis. Along the electron beam axis, the resolution is deteriorated by a factor of 1.15, due to the presence of the missing angular wedge in the recording of the data. Although the influence of this artifact on the reconstruction fidelity is quite complicated and requires a spatial frequency analysis, in order to minimize this effect that in first approximation induces an elongation of the object along the electron beam direction, a rescaling factor was calculated and applied to the corresponding volumes.

Quantitative 3D analysis of the particle faceting

Quantitative analysis of particle faceting is carried out as follows, using the DESK framework⁵⁹: First, each particle surface is extracted from its 3D volume and meshed using the ACVD software.⁶⁰ The result is a uniform triangular mesh with the number of vertices set to 10000, which provides a good trade-off between smoothness and accuracy given our sampling conditions. A normal is estimated for each vertex by averaging the normals of the triangles around the vertex. Then vertex normals are clustered in 20 classes using the K-means algorithm. In order to remove small non-planar regions, only the biggest clusters are kept. The result is a set of large planar regions. Finally, for each planar region, only the vertices with a normal deviating less than 20 degrees from the region average are considered as belonging to the flat region. This gives a robust vertex count for each planar region, and as the mesh is uniform, the number of vertices inside each planar region is a good approximation of the region area.

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We developed a geometrical approach allowing for the identification and subsequent quantification of nanoparticles crystallographic facets based on 3D data obtained by electron tomography. This approach which allows to automatically detects planar regions on particle boundaries and to assign them to crystallographic facets, was applied to palladium particles confined inside or located at the outer surface of a mesoporous silica shell. The influence of the encapsulation by silica on the morphological change of particles during an annealing treatment was investigated.

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