The Role of Nanocluster Aggregation, Coalescence, and Recrystallization in the Electrochemical Deposition of Platinum Nanostructures

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Supporting Information

ABSTRACT: By using an optimized characterization approach that combines aberration-corrected transmission electron microscopy, electron tomography, and in situ ultrasmall angle X-ray scattering (USAXS), we show that the early stages of Pt electrochemical growth on carbon substrates may be affected by the aggregation, self-alignment, and partial coalescence of nanoclusters of \( d \approx 2 \) nm. The morphology of the resulting nanostructures depends on the degree of coalescence and recrystallization of nanocluster aggregates, which in turn depends on the electrodeposition potential. At low overpotentials, a self-limiting growth mechanism may block the epitaxial growth of primary nanoclusters and results in loose dendritic aggregates. At more negative potentials, the extent of nanocluster coalescence and recrystallization is larger and further growth by atomic incorporation may be allowed. On one hand, this suggests a revision of the Volmer−Weber island growth mechanism. Whereas this theory has traditionally assumed direct attachment as the only growth mechanism, it is suggested that nanocluster self-limiting growth, aggregation, and coalescence should also be taken into account during the early stages of nanoscale electrodeposition. On the other hand, depending on the deposition potential, ultrahigh porosities can be achieved, turning electrodeposition in an ideal process for highly active electrocatalyst production without the need of using high surface area carbon supports.

INTRODUCTION

Over the past decade, fuel cell technology is among the most active fields of research and it is widely known that platinum is the most effective catalyst to facilitate both anodic and cathodic reactions in a proton-exchange membrane fuel cell.1 However, the efficiency of the oxygen reduction cathodic reaction is still a major challenge to achieve better performance at lower cost.1,2 Current fuel cell cathode catalyst standards consist of platinum nanoparticles supported on carbon materials of high surface area (Pt/C) and one of the ideal solutions to improve their performance is to tune their morphology at the nanoscale. Platinum nanostructures can be prepared by multiple methods which have been reviewed on many occasions,3 colloidal syntheses, and other solution based methods being the most common approaches to obtain nanostructures with high catalytic activity.4−6 Nonetheless, colloids are normally stabilized in solution by organic ligands and may undergo unwanted aggregation during deposition onto activated carbon. In both cases, their catalytic activity may be inhibited.7 In contrast, electrochemical deposition allows the growth of the nanostructures directly on the final support improving the electron pathway within the substrate, nanostructure, and electrolyte. Consequently, the technique has been proven effective to obtain highly active nanostructures8−10.

One of the key issues in achieving highly electroactive nanostructures in a reproducible way is to understand their formation mechanisms. However, despite the increasing number of publications in the field, the formation mechanisms are still under discussion. Nucleation and growth phenomena have been thoroughly studied for more than a century for colloidal synthesis,11 thin film growth12 and electrochemical deposition13 among others, resulting in the classic nucleation and growth theory which predicts that all formed nuclei will grow irreversibly by atomic addition until the reaction is halted. In colloidal synthesis, burst-nucleation/slow-growth14 and slow-nucleation/fast-autocatalytic-growth15 models have been used to understand nanocrystal synthesis. Both mechanisms differ in many aspects but share the concept that nanocrystal growth only proceeds by direct attachment, meaning reduction of metallic ions onto the surface of the growing particle. Consequently, the formation of highly electroactive nano-
dendrites has often been explained in such manner relating the fast autocatalytic growth process to the dendrite formation.\textsuperscript{4,5,16} Nevertheless, aberration-corrected high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) has recently become accessible for colloid chemists to provide new insights into nanocrystal generation.\textsuperscript{17} In addition, the development of technologies for in situ characterization has allowed following nanoparticle nucleation and growth in situ by transmission electron microscopy (TEM)\textsuperscript{18}−\textsuperscript{22} and small angle X-ray scattering (SAXS)\textsuperscript{22}−\textsuperscript{24} indicating that small nanoparticles grow by aggregation and coalescence to a bigger extent than by atomic addition. In fact, the formation of nanostructures by oriented attachment of nanocrystal building blocks has been reviewed recently\textsuperscript{25,26} and evidence of this growth pathway is shown also in the formation of many types of nanostructures.\textsuperscript{27}−\textsuperscript{29} Therefore, the idea that platinum and palladium electroactive nanodendrites are formed by the oriented attachment of small nanocrystals has been attracting more supporters recently.\textsuperscript{6,30,31}

However, electrochemical deposition has been traditionally studied considering nucleation and growth by direct attachment only.\textsuperscript{13} The fact that nucleation takes part on a surface has led to the assumption that nuclei stand still on the substrate. In the case of metal electrodeposition onto low-energy substrates, such as carbon, nuclei are supposed to grow radially by atom incorporation according to the well-known Volmer–Weber 3D island growth mechanism.\textsuperscript{13} However, it has been shown that classical models do not explain growth kinetics in detail.\textsuperscript{32}−\textsuperscript{34}

In some cases, platinum nanostructures with irregular morphologies have been electrodeposited,\textsuperscript{35}−\textsuperscript{46} but their growth mechanism is not yet completely elucidated, and several hypotheses have been proposed. Sometimes, dendritic growth in electrodeposition has been related to fast growth under diffusion control.\textsuperscript{47} In some cases, the appearance of globular particles has been related to secondary nucleation (Pt on Pt).\textsuperscript{35,39} In other cases, porous irregular morphologies have been related to spontaneous surface movement and aggregation of Pt nanoclusters.\textsuperscript{38,43} Alternatively, electrodeposited Pt nanostructures formed by the aggregation of elemental nanoclusters have been reported to present different shapes because of the the rate of H₂ evolution.\textsuperscript{35} Similar nanostructures have been reported by other authors without further discussion on the growth mechanisms.\textsuperscript{42,44}−\textsuperscript{46}

The understanding of the growth mechanisms in electrochemical deposition is behind other fields, mainly because of a lack of atomic-scale characterization. The fact that nucleation and growth occurs on the surface of an electrode has traditionally limited the characterization to nanoscale surface analysis techniques. In this case, the electrochemical growth of platinum nanostructures has been studied by atomic force microscopy (AFM),\textsuperscript{36,41,43} scanning tunnelling microscopy (STM),\textsuperscript{36,39} or field emission scanning electron microscopy (FESEM),\textsuperscript{37,59,41,44}−\textsuperscript{46} limiting the access to atomic-scale information. Some studies also include TEM characterization by using the extractive replica technique,\textsuperscript{36,39} in which the nanoparticles are removed from the electrode and placed on an electron transparent film for characterization. In these cases, although better resolution can be achieved, the process may alter the distribution of the particles over the electrode. Besides, nanostructures which are removed from one substrate and redeposited on another one may undergo aggregation or other unwanted processes during the postprocessing stage.

To overcome this situation, we have recently shown that by using carbon coated TEM grids (CCTGs) as electrochemical electrodes, we can access atomic-scale structural information on as-electrodeposited nanoparticles correlated with electrochemical measurements,\textsuperscript{48} and that a custom designed electrochemical flow cell allows studying nanoparticle growth in electrodeposition processes by in situ small angle X-ray scattering (SAXS).\textsuperscript{49} In this work, we study the electrochemical growth of platinum nanostructures onto carbon substrates by an optimized characterization approach, which combines in situ SAXS together with aberration-corrected HAADF-STEM and electron tomography. This way, we provide new insights into their growth mechanism and we show that nanostructures with ultrahigh surface area can be obtained by electrodeposition.

## RESULTS

### Cyclic Voltammetry

CV has been carried out on the system to establish the range of potentials in which the electrochemical reactions of interest happen. The blue curve in Figure 1a shows the first 6 scans of a CV recorded in a 1×10⁻³ M H₂PtCl₆ + 0.1 M KCl solution and CCTGs as working electrodes, at a scan rate of 50 mV/s. To understand the origin of the different peaks in the CV, the same electrode, a CCTG
with electrodeposited Pt (Pt-CCTG), is immersed in a solution of 0.1 M KCl, adjusted with HCl to have a pH of 2.5, similar to the Pt containing solution. The brown curve in figure 1a shows several scans of this Pt-CCTG electrode, at the same scan rate of 50 mV/s.

The blue curve shows the characteristic features of Pt electrodeposition from an acidic chloride solution. The first scan shows that the onset of platinum electrodeposition occurs at a potential around 0 V. In subsequent scans, platinum reduction starts at much more positive potentials, around 0.3 V. Besides, two cathodic peaks are visible at around −0.25 V and −0.45 V, and two anodic peaks show up at −0.16 and −0.34 V. The more negative peaks show the typical shape of a diffusion limited process and are ascribed to the proton reduction reaction, catalyzed by the Pt deposits on the CCTG. This is confirmed by the fact that the Pt-CCTG electrode shows the same peaks (brown curve) in a blank solution that contains the same concentration of free protons. Although not shown in the CV, H₂ evolution starts at around −0.75 V.

The interpretation of the less negative peaks is not that straightforward. The reduction peak at −0.25 V only shows up in a Pt containing solution so it must be caused by Pt electrodeposition. However, the inset on the lower side of figure 1a shows three small reduction peaks when the Pt-CCTG electrode is scanned in the blank solution. These peaks are due to hydrogen reduction reactions occurring on the Pt surface. The inset on the upper side of figure 1a shows only two visible oxidation peaks, shifted approximately 30 mV from the corresponding cathodic ones.

These cathodic and anodic peaks may be ascribed to hydrogen adsorption on platinum at different energies due the exposure of different crystallographic facets.56 To prove that, a series of CVs of Pt-CCTGs in the blank solution were performed at different scan rates, as shown in Figure 1b. Plots of the peak current densities VS scanning rate can be found in Figure S1 of the Supporting Information. The peak current density of the more negative peak (gray arrow) scales linearly with approximately the square root of the scanning rate, typical from diffusion controlled processes. However, the peak current densities of the three other peaks (black, green and blue arrows) scale almost linearly with the scan rate, typical from adsorption processes. Hence, it can be concluded that the latter represent adsorption/desorption processes on Pt. To further confirm this hypothesis, CVs were carried out in a Pt containing solution, on Pt-CCTGs with different amount of Pt. Figure S2 of the Supporting Information shows that for increasing amounts of deposited Pt, the contribution of the adsorption/desorption peaks increases, implying a reaction limited by the increasing surface of electrodeposited Pt.

**Ex Situ Characterization.** Electrochemical deposition experiments have been done by pulsing the electrode potential to various negative potentials. Spontaneous deposition of Pt nanoparticles was prevented by protecting the working electrode anodically.50,51 First, the resulting platinum deposits have been characterized by FESEM (see Supporting Information, Figures S3–S5). Nanoparticles of quasispherical shape are depicted in all the cases and particle size increases with increasing deposition time and decreasing overpotential whereas the opposite trend is found for particle number density. The use of CCTGs as electrodes, allows HAADF-STEM observations to be carried out on as-electrodeposited nanoparticles.54,48 Consequently, electron tomography is also feasible and, to the best of our knowledge, it is the first time that such approach is used to study electrodeposition processes.

**Electron Tomography.** Figure 2 shows visualizations of 3D reconstructions of representative nanoparticles after electrodeposition at −0.1 V for 20 s (a) and −0.6 V for 200 s (b). The morphology of Figure 2a is representative for nanoparticles obtained at E ≥ −0.2 V and this of figure 2b of nanoparticles obtained at E ≤ −0.4 V. Therefore, two regimes can be considered so hereafter, E ≥ −0.2 V and E ≤ −0.4 V will be referred as low and high overpotentials respectively. A set of movies providing more details of these reconstructions can be found in the Supporting Information. The most important feature is that the “nanoparticles”, far from being hemispherical islands as expected from conventional electrochemical growth, are ultraporous dendritic nanostructures which have branches in many random directions along the three axes.

This is in agreement with previous studies by FESEM,57 STM,58 or TEM,35 which had shown that Pt electrodeposition on carbon from a chloride solution resulted into rough shaped nanoparticles. Besides, the use of electron tomography enables us to perform three-dimensional quantitative analyses in the nanometer level. This provides interesting information related to the growth process and the properties of electrodeposited platinum. At low overpotentials, the structures have a very high degree of porosity (54%), and all branches have a similar thickness in the range between 1.6 and 2.5 nm. Figure 2a shows that many dendritic branches have spherical protuberances at their end, which are linked to the rest of the structure by a narrower stretch of material, or neck, typical from particle
coalescence processes.\textsuperscript{18−20,30,52} At high overpotentials though, the electrodeposited nanostructures are more compact and less porous (30%). The branches are not that easy to distinguish and have an average thickness which ranges from 2.8 to 4.9 nm.

**HAADF-STEM.** To get more hints on their formation mechanism, HAADF-STEM was used to observe representative nanostructures obtained at different overpotentials and deposition times. HAADF-STEM at low magnification shows that at high overpotentials, independent of deposition time, a population of nanoclusters of $d \approx 2$–4 nm coexists with larger nanostructures\textsuperscript{50} (see Supporting Information, Figure S6). Similar phenomena have been found to be related to nanocluster aggregation mediated growth in electrochemical

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**Figure 3.** High magnification HAADF-STEM images of platinum nanostructures obtained after electrodeposition at a potential of (a) $-0.2$ V for 20 s, (b) $-0.1$ V for 20 s, and (c) $-0.1$ V for 200 s. (d) Region revealing the presence of spherical protuberances linked by narrow necks. (e) Region showing several domains with different crystallographic orientation, together with the corresponding FFT shown as inset.

**Figure 4.** High magnification HAADF-STEM images and magnified regions of representative platinum nanostructures after electrodeposition at a potential of $-0.6$ V for (a and d) 3, (b and e) 20, and (c and f) 200 s.
deposition and colloidal syntheses. In contrast, only large dendritic structures are observed at low overpotentials.

Furthermore, Figure 3 shows representative high magnification HAADF-STEM images of nanostructures obtained at a potential of −0.2 V for 20 s (a), −0.1 V for 20 s (b), and −0.1 V for 200 s (c). Nanodendritic morphologies are depicted in all cases, consisting of many randomly oriented branches, which build up a quasi-circular shape and corroborate the same features which have been anticipated by the 3D reconstructions. Different deposition times do not influence the dendritic morphology. In all cases, many spherical protuberances of d ≤ 2 nm can be seen on the outer edges of the nanostructure, most of the times linked to the rest of the body by a narrower neck, as emphasized in Figure 3d. Even if lattice fringes extend coherently through large domains within the nanostructure, it is also clear that domains with different crystallographic orientation coexist within the same particle as shown by Figure 3e. The corresponding FFT, shown as an inset, confirms the polycrystallinity.

When deposited at high overpotentials, platinum nanoparticles also display an irregular porous shape but are more compact, in line with the three-dimensional electron tomography reconstructions (Figure 2b). Figure 4a–c shows that, in contrast with the case of low overpotentials, an increase in deposition time leads to more compact structures and smoother edges. After short deposition times, Figure 4a shows that many spherical protuberances are again connected to the body of the structure by necks as narrow as few atomic layers. These protuberances have an equivalent diameter of 2−3 nm, just as in the case of low overpotentials. After longer deposition times, Figure 4b and c shows that the nanostructures become more compact and with smoother contours. The detail in Figure 4f shows that after long deposition times, lattice fringes are coherent within larger domains. However, structural defects such as the twin planes emphasized in Figure 4d–f, or the open pores indicated by arrows in Figure 4c point again toward coalescence and recrystallization events.

In Situ Characterization. USAXS. To gain further insights into the phenomena occurring throughout the electrodeposition process, we have used in situ ultrasmall angle X-ray scattering (USAXS) and time-resolved SAXS to follow up nanoparticle size distributions and structural arrangements. Synchrotron (U)SAXS is well suited to perform in situ studies of electrodeposition systems as the attenuation of the incoming X-ray beam by the substrate and electrolyte must be overcome. Using the combined USAXS-pinSAXS setup available at 15-ID (Advanced Photon Source, U.S.A.), it is possible to obtain the scattered intensity, spanning over several decades in q (q = 4π (sin Θ/λ)), which can provide size and structural information from 1 nm to 1 μm. Further experimental details are provided in the experimental part.

Figure 5a shows combined USAXS−SAXS I(q) profiles obtained after the electrodeposition for 200 s at potentials of −0.1 and −0.6 V, together with their respective model fits. At high overpotentials (E = −0.6 V), two regimes can be clearly distinguished. The scattering at low q shows a power-law decay between q−2 and q−3, which extends from 6 × 10−3 to 10−1 Å−1. Such features are typical from scattering of agglomerates and are assigned to the scattering caused by the relatively compact porous structures shown in Figures 2b and 4. The scattering at high q shows a clear Guinier knee which can be related to the scattering of nanoclusters of few nanometers. This confirms that at high overpotentials, a population of isolated small nanoclusters coexist with larger aggregates, as indicated by low magnification HAADF-STEM (see Supporting Information, Figure S6). At low overpotentials (E = −0.1 V), a power decay between q−2 and q−3 extends in the mid q range from 2 × 10−2 to 10−1 Å−1. However, no clear Guinier knee is resolved at high...
Figure 6. Scheme of the electrochemical aggregative growth mechanism resulting into Pt nanostructures with different porosity depending on the deposition potential.

q indicating the absence of isolated nanoclusters, accordingly with low magnification HAADF-STEM observations. The knee observed at low q is caused by the scattering of the ultraporous dendrites shown in Figures 2a and 3. The scattered intensity from these structures cannot be modeled as a mass fractal agglomerate because of the sharp decay in q after the Guinier knee at q \(\approx 0.01 \text{ Å}^{-1}\), which exceeds q \(\approx 0.03 \text{ Å}^{-1}\). Three-dimensional electron tomography reconstructions (Figure 2a) and HAADF-STEM observations (Figure 3) reveal that the core of the dendritic nanostructures is denser than their outer shell. Therefore, as a first approximation, they are modeled as spheres with a solid core and porous55 shell, using the Debye equation for composite particles.56 An average dendrite diameter of 57 nm leads to a reasonable model fit, indicating that the selected model is a good approximation. Further details of the (U)SAXS data reduction and model fits are provided in the Supporting Information.

Time-Resolved SAXS. Pinhole SAXS frames can be obtained every second with a reasonable signal-to-noise ratio, so time-resolved data acquisition is also possible. Figure 5b shows the evolution of the \(I(q)\) profile with time when a potential of −0.6 V is applied. Ten 1-s frames have been averaged each time for the sake of clarity. The most important feature is that the shape of the Guinier knee at high q does not change with time, indicating that isolated nanoclusters do not grow with deposition time. Otherwise, this feature would clearly shift to smaller q values.22,57 To estimate the average particle size, scattering data is modeled as a distribution of monodisperse spheres accounting for interparticle interference. As anticipated by the time-resolved \(I(q)\) profiles, the inset in Figure 5b shows that primary nanocluster diameter is constant over deposition time. Figure 5c shows the dependence of nanocluster size on deposition potential. Red markers represent particle size derived from the SAXS model, whereas black ones are taken from the evaluation of spherical protuberances from HAADF-STEM at higher magnification, and blue ones from the evaluation of isolated nanoclusters by HAADF-STEM at low magnification. A good agreement between both techniques is found as SAXS data indicates a nanocluster size of \(d \approx 1.8 \text{ nm}\) and HAADF-STEM analysis indicates \(d \approx 2 - 3 \text{ nm}\).

DISCUSSION

Growth Mechanism. By the combined analysis of in situ (U)SAXS and HAADF-STEM, we can get new insights into the growth mechanism of the electrodeposited platinum dendritic nanostructures.

Sometimes, dendritic growth has been associated to diffusion limited growth.47 However, at low enough overpotentials, diffusion cannot be considered the rate determining step and still ultraporous dendritic features are obtained (Figure 2a). In addition, pure epitaxial growth can be ruled out in the cases that spherical protuberances are linked through narrow necks (Figures 3b and 4a),18–20,30,52 that domains with different crystalllographic orientation coexist (figure 3c),6,25,27,30,52 or that structural defects such as twin planes or stacking faults are abundant (Figure 4),30,52 as all these features indicate cluster coalescence events. At high overpotentials, the coexistence of large nanostructures with isolated nongrowing small nanoclusters, indicated by ex-situ HAADF-STEM at low magnification and in situ SAXS, suggests again nanocluster aggregation mediated growth.26,27,29,34 Accordingly, dendrite branch thickness, spherical protuberances and isolated nanoclusters have the same dimensions (\(d \approx 2 \text{ nm}\)), regardless of applied potential and deposition time. Hence, experimental observations suggest that the electrochemical deposition of platinum onto carbon substrates results into ultraporous nanodendrites formed by the aggregation and partial coalescence of Pt nanoclusters of \(d \approx 2 \text{ nm}\).

This is an important concept to take into account as metal electrodeposition has traditionally been considered to proceed by nucleation and direct attachment. Nanocluster surface diffusion and aggregation have barely been considered in electrochemical nucleation and growth studies because of the assumption that growing nuclei would be pinned on the surface and motionless. However, in the case of Pt electrodeposition, several groups have found irregular and rough nanostructures and suggested that cluster aggregation,34,8,35,58 or secondary nucleation1 could be taking part. Besides, we reported recently that silver electrodeposition on carbon proceeds by an electrochemical aggregative growth mechanism which takes nanocluster surface diffusion and aggregation into account.34 Generally, nanocluster diffusion coefficients are found to differ in several orders of magnitude depending on the substrate-cluster interaction.58,59 If the mismatch between the lattice parameters of the substrate and the cluster is small, nanoclusters have been found to have very small diffusion coefficients.59,60 However, provided that the mismatch is large enough, nanoclusters of few nm have been reported to display large diffusion coefficients.39,61 Moreover, proofs of nanocluster surface diffusion upon electrochemical cycling exist.62–64 Therefore, it is plausible to consider that electrodeposited platinum nanoclusters of \(d \approx 2 - 3 \text{ nm}\) could be mobile over a carbon surface, leading to a growth mechanism mediated by cluster aggregation and coalescence. Such mechanism is schematized in Figure 6.
At low overpotentials, regardless of deposition time, small and large dendritic structures have branches of similar thickness of about $2^{-3}$ nm, the same dimensions as the spherical protuberances obtained by high magnification HAADF-STEM. This indicates that even at later stages of the electrochemical deposition process, large nanostructures seem to keep growing by the addition of clusters of the same size, as pictured by the growth pathway at the top of Figure 6. This in turn indicates that a self-limiting growth mechanism stops the epitaxial growth of primary clusters and dendritic aggregates. Although traditionally, it has not been thoroughly discussed in the electrochemical deposition field, self-terminating or growth inhibiting mechanisms have been recently reported in the cases of Pt electrodeposition on Au$^{65}$ or Ni electrodeposition on TiN.$^{66}$ It must be noted that dendritic structures also extend in the direction perpendicular to the substrate (see Figure 2 and videos in Supporting Information), so nanocluster detachment from the surface or secondary nucleation (Pt nucleation on Pt), followed by nanocluster diffusion over the platinum structure may be happening as well.$^{37}$ Such process points again toward the existence of a self-limiting growth mechanism, that favors the formation of new clusters onto the platinum surface rather than epitaxial crystal growth. Some crystallographic domains extend beyond primary nanocluster size due to nanocluster oriented attachment$^{25}$ or self-alignment and partial coalescence.$^{6,27,30,52}$ However, other crystallographic domains are as small as the primary particle size (Figure 3e), leading us to believe that such self-alignment and partial coalescence is not a spontaneous process but happens under electrochemical polarization. Nonetheless, in this range of potentials, the extent of coalescence is limited because even after very long deposition times, the nanostructures conserve ultrahigh porosity and large surface area. This in-turn provides exciting possibilities for the engineering of highly active electrocatalysts, where nanoporous three-dimensional structures are an ideal solution.

At high overpotentials though, the situation is slightly different, as shown by the growth pathway at the bottom of figure 6. After long deposition times, the electrodeposited nanostructures are more compact, less porous and their lattice fringes extend over very large domains, indicating that they have undergone a higher degree of recrystallization and epitaxial growth by atomic incorporation. First, this indicates that recrystallization kinetics are potential dependent and are accelerated in this potential range. Second, this indicates that a certain degree of nanocluster coalescence is needed to overcome the self-limiting growth mechanism and allow further growth by atomic incorporation.
One possible explanation for the dependence of nanocluster coalescence processes on the deposition potential may be related to specific adsorption and hydrogen reduction processes. We have observed that nanocluster aggregates undergo recrystallization for \( E \leq -0.4 \) V, whereas they do not for \( E \geq -0.2 \) V. Cyclic voltammetry (see figure 1) shows that for \( E \leq -0.4 \) V, platinum deposition occurs simultaneously with proton reduction. Contrarily, for \( E \geq -0.2 \) V, platinum deposition occurs only with a small extent of hydrogen adsorption on some specific facets. Although it is unlikely in the potential window considered in this work, it has also been shown that chloride specific adsorption may hinder the growth of Pt NPs. It is therefore logical to think that the interplay of different adsorption and catalytic processes on the platinum surface may influence nanocluster self-limiting growth and coalescence. Hence, it could be possible that at low overpotentials the adsorption of hydrogen limits the growth of Pt nanoclusters, similarly to the self-terminating growth of Pt films onto Au. Proton reduction reactions could favor coalescence processes instead.

Another possible explanation is based on the fact that coalescence and recrystallization processes are driven by the concentration of free metal ad-atoms on the nanocluster surface. In an electrochemical deposition experiment, the concentration of free ad-atoms on the surface increases when large cathodic overpotentials are applied. Hence, faster coalescence and recrystallization kinetics could be induced by cathodic polarization. In other cases, electrochemical potential driven nanocluster surface diffusion and coalescence have been detected under large anodic polarization in electrolytes not containing the corresponding metal ions. Such cases could be explained by the same hypothesis, as a large concentration of free atoms on the surface would have been stripped off the metal clusters themselves by the application of large anodic potentials.

The fact that the self-limiting growth mechanism may vanish after a certain degree of nanocluster coalescence and recrystallization is based on the observation that epitaxial growth contributes to the growth of larger structures only after recrystallization (Figure 4c). However, primary nanoclusters and loose dendrites do not seem to grow by atomic incorporation substantially. Similar phenomena have been sometimes attributed to closed-shell magic sizes and have been reported in colloidal nanoparticle synthesis and in silver electrodeposition.

Assuming that platinum primary nanoclusters do not grow by atomic addition, that a certain degree of recrystallization is needed to overcome the self-limiting growth mechanism, and that recrystallization is dependent on the electrochemical potential, these features should be reflected by electrochemical measurements. Figure 7a shows a set of successively recorded CVs of the electrochemical reduction of Pt on GC electrodes from the same solution used throughout this work. The first CV consists of a fresh GC electrode cyclized from 0.7 V to 0 V, and subsequent CVs are measured using the same electrode and increasing cathodic limits, \( E_{Cath} \) from -0.1 to -0.7 V. For comparison, the dashed lines correspond to the CV recorded on a fresh CCTG (Figure 1a).

It can be seen that the platinum reduction onset shifts to more positive values after an increasing number of scans with increasing cathodic limit, until it stabilizes around 0.3 V. This is typical from CV studies of the electrodeposition of a metal on an low-energy substrate. In these cases, the first scan shows a reduction onset being more negative than the standard redox potential due to the need of extra energy (overpotential) to compensate for the creation of new metal-substrate and metal—electrolyte interfaces. Subsequent scans show a shift in the reduction onset to more anodic potentials as not all the metal is stripped off in the anodic sweep and hence the metallic ions reduce over the metal itself without the need of a large overpotential.

However, if we look at the detail shown in Figure 7b, we can see that when \( E_{Cath} \geq -0.2 \) V, the onset of Pt reduction remains almost constant around 0.1 V and does not show a significant anodic shift. This may indicate that, when deposited in this potential range, Pt deposits do not act as preferred nucleation sites in which more Pt is reduced at lower overpotentials. This correlates with the fact that in this range of potentials, Pt nanoclusters exhibit a self-limiting growth mechanism that hinders their growth by direct attachment. On the other hand, if we look at the detail shown in Figure 7c, we observe that when \( E_{Cath} \leq -0.3 \) V, the onset of Pt reduction gradually shifts toward more positive values, as expected when a metal deposition occurs over the metal itself at lower overpotentials. At the same time, 2 distinctive regions are also gradually established in the voltammogram. A first cathodic plateau is followed by a current increase and a cathodic peak. Although a clear explanation about the distinction between these regimes is missing at the moment, it is clear that when \( E_{Cath} \leq -0.3 \) V, Pt reduction gets facilitated. This correlates again with the fact that in this range of potentials, the self-limiting growth mechanism has vanished, nanocluster coalescence and recrystallization have proceeded, and growth by direct attachment occurs (Pt deposition on Pt). Thus, the growth mechanism inferred from HAADF-STEM, electron tomography and in situ (U)SAXS, correlates with the evaluation of the electrochemical data.

**Electrodeposited Nanostructures with Large Surface Area.** Highly porous nanostructures with large surface areas are ideal for several applications including fuel cells. Current fuel cell cathode catalyst standards consist of platinum nanoparticles supported on carbon materials of high surface area (Pt/C) and have a mass-specific surface area (MSA) around 30–90 m²/g Pt. Recently, a lot of effort is continuously being devoted to improve these standards by different approaches. One of them is to improve their performance and cost effectiveness by increasing their MSA and their ratio from real to geometric area (RRG). Therefore, tuning their morphology at the nanoscale is the ideal solution. In this context, nanoparticle agglomerates, dendritic nanostructures or meso-structured platinum thin films provide enhanced electrocatalytic activity because they conserve their size-specific properties, while they form threedimensional nanostructures with a high surface area and a high concentration of surface defects. Because of their three-dimensional nature, these approaches provide a much higher RRG and thus eliminate the need for high surface area carbon supports, that can degrade quickly under operating conditions. In addition, these structures do not suffer from active area loss due to agglomeration under operating conditions, as it is the case for supported nanoparticles.

To determine the active surface area of supported Pt nanostructures, several indirect approaches are available, being hydrogen underpotential deposition the mostly used. However, it has been shown that these methods may show large deviation from the real surface area. Alternatively, measuring surface areas in a direct manner by high resolution...
microscopy would be more accurate. However, two-dimensional projections can only be used for this matter if the particle shape is simple (i.e., sphere, cube). Instead, electron tomography allows to compute these properties in particles of any shape. Therefore, the technique is of great interest to get exact quantitative information of irregular and dendritic Pt nanostructures.

In our case, computed MSAs from the three-dimensional reconstructions are 68.06 and 41.96 m²/gpt for nanostructures electrodeposited at low and high overpotentials respectively. As shown in Figure 8a, these values are similar to commercial standards consisting of nanoparticles of r ≈ 2 – 3 nm. However, one of the problems of supported small nanoparticles is that they do not provide RRGs large enough unless they are supported on porous carbon supports, as shown by Figure 8b. Alternatively, the obtained dendritic nanostructures present ratios around 6.7 and 4.2 for low and high overpotentials respectively. In the first case, such ratio is similar to this of mesoporous films and only a bit smaller than commercial Pt/C catalysts over high surface area carbon supports.

![Figure 8](image)

**Figure 8.** Plots of calculated (a) mass-specific surface area (MSA) and (b) ratio from real to geometric area (RRG) VS particle radius of nanostructures electrodeposited at low (blue) and high (green) overpotentials. Gray lines are calculated values for nanoparticles supported onto a flat electrode. Red and black lines represent values obtained from mesoporous films and commercial Pt/C catalysts over high surface area carbon supports respectively.

as shown by the dotted lines in Figure 8b. Details of the calculations are provided in the Supporting Information.

In addition, the atomic-scale information obtained by the use of aberration-corrected HAADF-STEM shows also that the electrodeposited nanostructures are enclosed in many cases by high index planes, such as these indicated in Figure 4e. Similar structures have been reported in colloidal syntheses and have been proven to exhibit enhanced catalytic activity compared to low-index facets.

Because of the aforementioned reasons, electrodeposited Pt nanostructures have an incredible potential for fuel cell technology as they may display ultrahigh surface areas, conserve size-specific properties of small nanoclusters, be large enough to avoid aggregation, and not need high surface carbon supports which degrade under operating conditions.

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**CONCLUSIONS**

By using an optimized characterization approach that combines FESEM, aberration-corrected HAADF-STEM, electron tomography and in situ (U)SAXS, we show that the electrochemical growth of Pt on carbon substrates may be affected by the aggregation, self-alignment and degree of coalescence and recrystallization of nanoclusters of d ≈ 2 nm. The size of the primary nanoclusters is independent of deposition time and overpotential. However coalescence and recrystallization kinetics are dependent on the deposition potential and they influence later growth stages. At low overpotentials, a self-limiting growth mechanism may block the epitaxial growth of primary nanoclusters, so loose highly porous dendritic aggregates are formed. At more negative potentials, more compact and less porous nanostructures are obtained. In the latter case, the extent of nanocluster coalescence and recrystallization is larger, the self-limiting growth mechanism vanishes, and further growth by atomic incorporation may be allowed. This leads to suggest a revision of the classical Volmer–Weber 3D island growth mechanism. In addition to direct attachment, nanocluster self-limiting growth, surface diffusion, aggregation and coalescence may need to be considered as important processes of the early stages of nanostructure growth.

In addition, electron tomography and HAADF-STEM have proved very useful to characterize surface properties of electrodeposited Pt. Depending on the deposition potential, ultrahigh porosities can be achieved, leading to very high MSAs and RRGs, turning electrodeposition in an ideal process for highly active electrocatalyst production without the need of using high surface area carbon supports. The possibility to obtain ultraporous dendritic nanostructures by nanocluster aggregation in an electrochemical deposition route opens up a new and exciting set of possibilities to engineer supported nanostructures with nanoclusters as building blocks.

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**EXPERIMENTAL SECTION**

**Electrochemistry.** All experiments have been carried out using a solution of 1 × 10⁻³ M H₂PtCl₆ + 0.1 M KCl previously deareated by N₂. Electrochemical measurements have been performed using AUTOLAB PGSTAT 100 and a IVIUM Compactstat potentiostats in a three-electrode configuration with an Ag/AgCl reference electrode and a Pt counter electrode. All the potentials mentioned throughout the paper are referred to Ag/AgCl.

**Ex Situ Characterization: FESEM and HAADF-STEM.** To perform TEM analysis on as-electrodeposited nanoparticles, CCTGs from EMS (300mesh, CF 300Au) have been used as electrochemical working electrodes as described elsewhere. Ex-situ low-resolution
morphological characterization of the electrodeposited nanoparticles has been performed using a JEOL JSM-7000F FESEM operated at 20 kV. Electron tomography experiments were carried out using a FEI Tecnai G20 electron microscope operated at 200 kV. A Fischione tomography holder (model 2020) was used and the series were acquired automatically using the Xplore3D software (FEI). Both tilt series were acquired in HAADF-STEM mode with an angular range from −68° to +70° and a tilt increment of 2°. The alignment of the series was done inInspect 3D software (FEI). 3D reconstruction was performed using the Simultaneous Iterative Reconstruction Technique (SIRT) as implemented in Inspect 3D. The visualization of the reconstructions was done in Amira S.4.0 software package from Mercury computer systems. Aberration-corrected HAADF-STEM images were acquired using a double aberration corrected FEI Titan 50–80 electron microscope operated at 300 kV.

In Situ Characterization: (U)SAXS. To perform in situ (U)SAXS measurements, 180 μm thick glassy carbon pieces (HTW-Germany) have been used as working electrodes in a custom designed transmission cell in order to obtain simultaneously electrochemical and SAXS data during Pt electrodeposition. The sample cell is essentially the same as used previously19,75,74 and a schematic illustration of the sample cell, as placed on the beamline, is shown elsewhere.8 Using this setup, we were able to obtain the scattered intensity from the deposited nanoparticles by first obtaining the background scattered intensity from the electrolyte and substrate. Then, The electrode potential was pulsed to different negative potentials for 200s while in situ pinSAXS images were simultaneously collected every second. Synchronization between the SAXS data collection and potentiotstat was accomplished using triggering commands, available in the Ivium software. Right after the initial electrodeposition pulse was completed, USAXS data was collected in situ in open circuit potential. All small-angle X-ray scattering experiments were performed at the Advanced Photon Source (APS), beamline 15-ID. The sample cell was exposed to a 16.8 keV beam. The electrodeposition pulse was completed, USAXS data was collected immediately thereafter, and then a 10−4−10−3 Å−1. All subsequent data reduction was performed in the Irena package, available for Igor pro.75

**REFERENCES**


