Review Article

Current atomic-level understanding of electrochemical nucleation and growth on low-energy surfaces

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Abstract

This review presents recent progress in the understanding of electrochemical phase formation on low-energy substrates, which is essential for metal electrodeposition and the design of stable batteries. Advanced characterization techniques and ultrasensitive electrochemical instrumentation give access to experimental data that were not available a few years back. Besides, the continuous development of theoretical models gradually provides a more complete description of multiple nucleation. However, important contradictions between experimental findings and theoretical formulations are found: nonclassical growth pathways, single-atom critical clusters, and cluster densities that are orders of magnitude higher than the calculated number of active sites. New descriptions of the initial steps of nucleation are discussed. They are grounded on nucleation being a nonactivated process, in which the initial stages of phase formation could involve simply adsorbed atoms collapsing into larger clusters driven by minimization of the overall interfacial energy. Finally, some remaining challenges and possible research directions are outlined.

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Introduction

A good knowledge of electrochemical phase formation is paramount for technologically important processes, such as the electrodeposition of metals on foreign surfaces or the stability of batteries upon electrochemical cycling. The topic is an active subject of research for more than a century. The understanding of electrochemical nucleation and growth, from the atomic level to the macroscale, has progressed enormously, thanks to the advances in electrochemical and analytical instrumentation. However, despite decades of dedicated theoretical and experimental studies, the quantitative description of the nucleation and growth of multiple nuclei remains incomplete.

The theoretical foundations of electrochemical phase formation [1,2] have been recently reviewed [3–5]. It is generally agreed that electrodeposition on a foreign substrate occurs by a process of nucleation, through which ions in solution discharge over active sites on the surface, that is, steps, kinks, holes, grain boundaries, chemically modified locations, etc. Depending on the size of the critical nucleus, n_C, which depends on the overpotential, η, nucleation can be described either by a classical or an atomistic approach [2–5]. The study of the kinetics of nucleation consists, thus, in deriving the dependence of nucleation rate on supersaturation. A first approximation considers a stationary nucleation rate J_{ST}, assumed to be first order with respect to the number of active sites on the surface, N_0. The study of multiple nucleation [6–11] considers that there is a number of energetically identical active sites which is instantaneously fixed upon application of a given η. Under these assumptions, during nucleation and growth, the number of active sites would decrease with time only because of two reasons: the nucleation itself (i.e., occupation of active sites by nuclei) and the spreading of zones of reduced concentration and overpotential around growing stable clusters [12]. Growth of the new phase is traditionally seen as to proceed by the stepwise addition of atomic or molecular species: either by incorporation of mobile adsorbed adatoms or by direct attachment of ions from solution.

However, it is admitted that such models for multiple nucleation and growth are not complete yet [4,5,12]. First, time-varying (nonstationary) and site energy–dependent (heterogenous) nucleation rates should be used. Second, the concept of active site is still under discussion: active sites may appear or disappear from the electrode surfaces simultaneously with the nuclei of the

new phase, owing to adsorption/desorption or oxidation/reduction processes. This makes it difficult to distinguish between the actual nucleation rates and the rates of appearance and disappearance of active sites [13]. Third, recent experimental findings (see below) indicate that growth can occur also by other nonclassical pathways.

This review gives an overview of the most recent progress in the area. First, innovative experimental approaches, helped by the advent of nanoscale characterization techniques and ultrasensitive electrochemical instrumentation, have given access to experimental data, which were not available a few years back. Second, the continuous development of analytical and numerical models gradually provides a more complete description of the electrochemical nucleation and growth process, which enables a more consistent way of interpreting experimental evidence. Finally, some of the remaining challenges and possible research directions in the area will be outlined.

Recent experimental findings on the early stages of electrochemical nucleation and growth on low-energy surfaces

Electrochemical nucleation is strongly dependent on metal-to-substrate interaction. When the latter is high (metal on metal), phase formation generally begins by the formation of a 2D metal monolayer, which further grows layer by layer or exhibits a transition to 3D growth [14]. On the contrary, when metal nucleation takes place on nonmetallic electrode materials (low-energy surfaces), such as carbon or oxides, nucleation and growth of 3D islands is assumed. For metal on metal deposition, electrochemical scanning tunneling microscopy (EC-STM) delivers atomic-scale resolution [15] in electrochemical deposition on single crystals [14,16,17]. For deposition on low-energy substrates, atomic-resolution data are scarce owing to the nonneglectable roughness and structural surface heterogeneities. This review concentrates on the latter case, which is highly interesting for the field of energy conversion and storage.

The most accessible approach to study the electrochemical formation of a new phase on a low-energy substrate is to record the current−time transient (CTT) during a potentiostatic experiment, followed by *ex situ* evaluation of the morphology of the deposit at different times, by means of scanning electron microscopy(SEM) and, more recently, transmission electron microscopy (TEM). A way to get direct access to TEM resolution on as-electrodeposited nuclei is by using carbon-coated TEM grids (CCTGs) as electrochemical electrodes [18]. Our results on silver [19] and platinum

[20] deposition have provided strong evidence that the early nucleation and growth process is much more complex than what is assumed in the formulations of multiple nucleation [6−11]. We suggest that (1) growth inhibition at the nanocluster level, (2) surface mobility of small nanoclusters ($d \sim 1 - 3 \ nm$), and (3) aggregation and coalescence, hereby denoted as nonclassical growth pathways, are important elementary steps of the electrochemical growth process (Figure 1a) [19−21]. In relation to analogous phenomena in solution-based nucleation and growth [22,23], we integrate these growth pathways within an electrochemical aggregative growth mechanism [21].

More recently, using thin enough boron-doped diamond electrodes, identical-location scanning TEM has allowed tracking of Au electrodeposition from a single atom to a crystalline nanoparticle (NP) [24]. These studies provide direct evidence of other nonclassical pathways: potential-induced atom movement, atom clustering, and cluster transformation into crystalline NPs via gain or loss of atoms (Figure 1b).

A less accessible but more efficient approach is the use of liquid electrochemical TEM holders for *in situ* (S) TEM investigation of early phase formation [26,27]. In this way, CTTs can be recorded simultaneously with TEM images. These studies show that the cluster density determined from TEM videos is 3 orders of magnitude greater than that calculated from the model fit [28]. *In situ* electrochemical (S)TEM (EC-(S)TEM) has also been used to study Pd electrodeposition on carbon, where the evidence suggests that an electrochemical aggregative growth regime also operates [29]. Although the reproducibility and data interpretation are still limited owing to the strong interaction of the electron beam with the electrolyte [30], recent studies foresee strategies to mitigate measurement artifacts [31]. However, the scattering of the electrolyte also limits the resolution of a typical liquid cell TEM experiment: the smallest measured islands have diameters about $30 - 50 \ nm$ [28,29,32]. This impedes so far a direct comparison with *ex situ* (S)TEM, where nanoclusters of $d \sim 1 - 3 \ nm$ can be imaged [19−21,24].

More recently, Cu deposition on indium tin oxide (ITO) has been investigated by high-speed lateral molecular force microscopy (HS-LMFM) with unprecedented spatiotemporal resolution (subsecond image acquisition) and extremely low probe-surface interaction [25]. These studies unveil again a scenario linked to nonclassical growth pathways: a highly dynamic environment before the formation of stable nuclei, featuring nucleation/dissolution events and growth via a 2D aggregation process (Figure 1c).

Figure 1
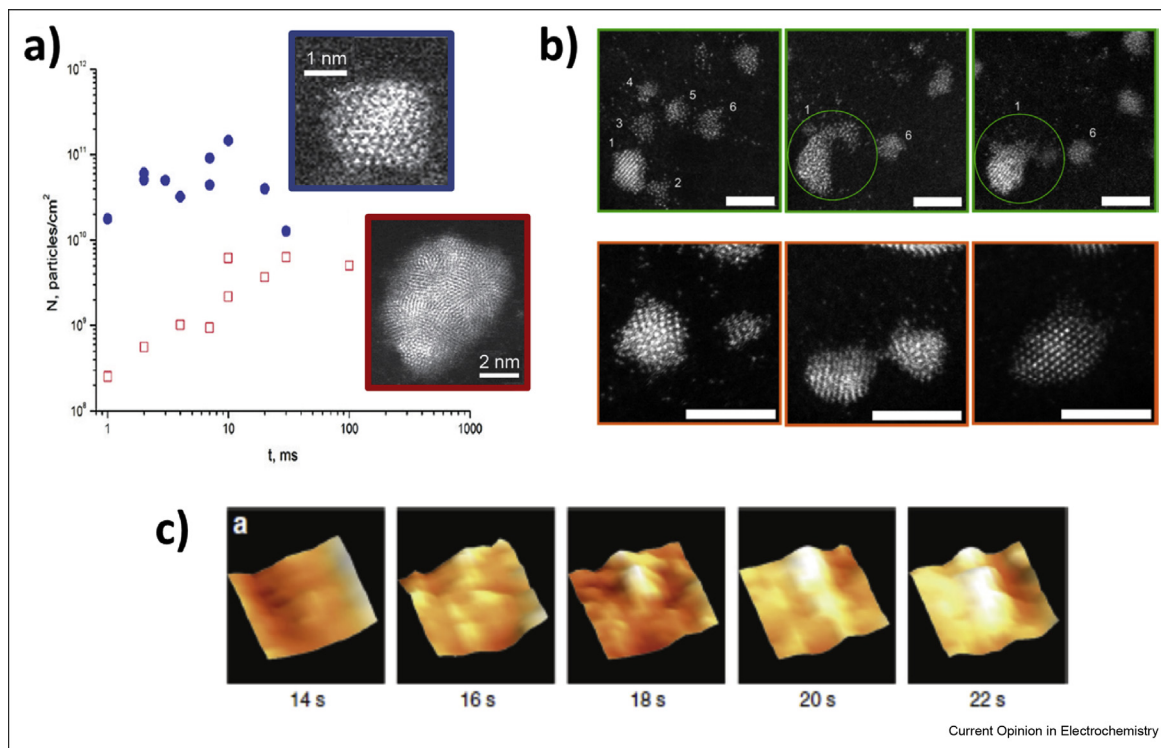
Recent experimental findings that highlight the importance of nonclassical growth pathways. **(a)** Time evolution of the number density of Ag NPs during deposition on CCTGs: small nanoclusters of $d{\sim}1{-}2$ nm (blue) are formed during deposition but aggregate to form polycrystalline NPs with $d > 6$ nm (red). Adapted with permission from the study by Ustarroz [19], copyright 2012, American Chemical Society. **(b)**. IL-STEM images show dynamic interactions between NPs during Au electrodeposition: growth times of 5, 10, and 30 ms. Scale bar is 3 nm. Reprinted with permission from the study by Hussein [24], copyright 2018, American Chemical Society. **(c)** Birth and growth of a copper nucleus evidenced by *in situ* HS-LMFM scans (46×46 nm^2 regions), taken from 14 to 22 s after a potential step. Reprinted with permission from the study by Harniman et al [25], copyright 2017, Nature Publishing Group. CCTGs, carbon-coated TEM grids; TEM, transmission electron microscopy; NPs, nanoparticles; IL-STEM, identical-location scanning TEM, HS-LMFM, high-speed lateral molecular force microscopy.

Recent advances in analytical and numerical modeling of electrochemical nucleation and growth

Despite solid theoretical foundations [1,2], some of the experimental findings outlined previously indicate that the theoretical description of the electrocrystallization process needs to include, stepwise, higher degrees of complexity. Recent developments include more accurate descriptions of the nucleation rate [33,34], numerical modeling strategies for the electrochemical growth of single [35,36] or multiple [37] clusters, and extensions of the analytical formulation of the CTTs for multiple nucleation under potentiostatic control [38,39].

Most theoretical formulations consider (1) single-step ion discharge reactions and (2) the formation of hemispherical nuclei. However, first, electrodeposition may also proceed by multiple-step discharge reactions and, second, the nucleus wetting angle depends on the surface and adhesion energies. Recent studies have shown

that a wrong consideration of any of these concepts leads to considerable errors in the determination of nucleation rate, growth kinetics, and current—time relationships [33,34].

Moreover, despite not capturing all the nuances of the nucleation and growth process, the use of CTTs to obtain thermodynamic and kinetic parameters is very practical. Nowadays, the early analytical formulations of multiple nucleation [6—11] are extended (Figure 2a) to include prenucleation ion discharge [40,41], electrocatalytic reactions (proton reduction, etc.) on growing centers [40,41], mixed kinetics [41—43], and wetting angle [44]. Besides, more recently, a numerical model [38] and an analytical approximation [39] have been developed for mixed kinetics. The model has also been expanded to include the prenucleation regime and coreduction [45].

Over the years, it has been found that J_{ST}, $N(t)$, and N_0 obtained experimentally from surface analysis (J_{ST-EXP},

Figure 2
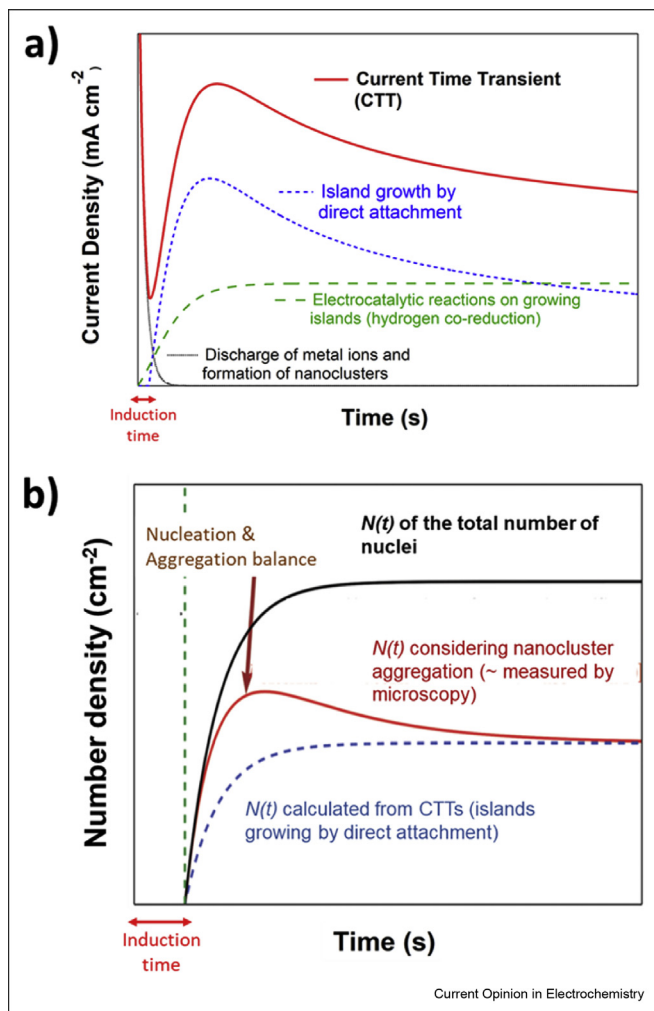
Advances in the theoretical description of multiple nucleation. **(a)** Contributions of different processes to the CTTs (red): prenucleation ion discharge and formation of small nanoclusters (black); growth of stable islands by direct attachment considering the wetting angle, the induction time and mixed kinetics (blue); and electrocatalytic reactions at the surface of the growing islands (green). **(b)** Schematic representation of different $N(t)$: the total number of nuclei (black); the total number of clusters considering aggregation (red); and the incorrect number of nuclei that would be determined from the model fit of a CTT. Adapted with permission from the study by Mamme et al [37], copyright 2018, The Royal Society of Chemistry. CTTs, current–time transients.

$N(t)_{EXP}$, and N_{0-EXP}) may be several orders of magnitude higher than those obtained from the CTTs (J_{ST-CTT}, $N(t)_{CTT}$, and N_{0-CTT}) [19,21,28,41,46,47]. Therefore, some important clarifications related to the interpretation of these data are needed.

First, all multiple nucleation models assume a stationary nucleation rate J_{ST}, whereas the nucleation rate should be described as site- and time-dependent $J(s,t)$ [12]. Second, the models do not consider the appearance or

disappearance of the active sites during nucleation [4,13]. Third, even in the case that the CTT provides estimates of N_{0-CTT} and J_{ST-CTT} in line with microscopical observations, the resulting kinetic constant may be orders of magnitude lower than this determined from Tafel analysis in an appropriate experiment [45]. This could be related to an inhibition of direct attachment (by hydrogen adsorption [20,48,49] or hydroxide formation [50,51]) in favor of other growth pathways [20,21,49]. Fourth, all multiple nucleation models assume that all nuclei are fixed to a surface site and grow only by the stepwise attachment of atomic or molecular species. However, $N(t)_{CTT}$ does not represent the number of nuclei, but only the number of particles growing through direct attachment, which may be orders of magnitude lower than that of the original nuclei (Figure 2b), due to growth inhibition [20,48−51], nanocluster mobility and aggregation [19,21,25,37], NP detachment from the surface [47,52], and other interactions between neighboring growing centers [24]. Deviations between N_{0-EXP} and N_{0-CTT} could possibly be related to any of these phenomena.

For example, for long enough deposition times, if J_{ST-EXP} and N_{0-EXP} are orders of magnitude higher than J_{ST-CTT} and N_{0-CTT}, it is highly likely that growth by direct attachment is inhibited [20,21]. Alternatively, for short times, if J_{ST-EXP} is much higher than J_{ST-CTT}, it may also mean that clusters of many atoms undergo surface diffusion and aggregation [19], whereas similar values for J_{ST-EXP} and J_{ST-CTT} would imply that surface diffusion is limited to adatoms or clusters of a few atoms. The latter case generally leads to CTTs with longer induction times [37], however these CTTs can also be encountered when growth is controlled by mixed kinetics [38]. These few examples highlight that CTT analysis is a valid preliminary step for the study of electrochemical nucleation and growth but remains insufficient. The reason is that CTTs represent a convolution of multiple elementary processes and, therefore, different growth pathways may still lead to identical transients. However, a proper interpretation of the CTTs, combined with surface analysis provides very valuable information about the classical and nonclassical growth pathways taking place.

Because CTTs allow determining J_{ST} (admitting the incompleteness of the models, see above), the critical size for nucleation, n_c, and the nucleation energy, $\Delta G(n_c)$, can be calculated from the slope of the $ln(J_{ST})$ vs η relation [2,4]. Many studies report values of n_c of few atoms [1,2]. More specifically, recent works estimate $n_C = 0 - 1\ atoms$ and $\Delta G(n_c)$ as small as $1 - 10\ kJ\ mol^{-1}$, which depicts electrochemical nucleation as a nonactivated process [41,53−55]. In this scenario, the initial stages of the formation of a new phase could involve a submonolayer of adsorbed atoms, which collapse into larger clusters driven by minimization of

the overall exposed area, and consequently of the interfacial energy. This has been lately discussed in terms of spinodal decomposition [12,53,54] or of an electrochemical aggregative growth mechanism [19–21,37].

Nevertheless, one should remember that n_c and $\Delta G(n_c)$ are calculated from J_{ST} (η) being determined from fitting the CTTs to a multiple nucleation model, and, as explained previously, such J_{ST-CTT} does not necessarily represent a nucleation rate, but the rate at which nonmoving clusters, which grow under direct attachment, are formed [19–21,37]. Further experimental approaches, such as in situ EC-(S)TEM [28] and/or multiscale computer simulations [37], are required to validate the previous assumptions and to determine J_{ST}, or $J(s,t)$, from a complementary microscopic approach.

Electrochemical nucleation and growth of single entities

Another interesting approach, developed over the last few years, is to measure CTTs of a reduced number of growing nuclei, down to the single-entity level. This approach may be of interest to evaluate the heterogeneity of both the activity of the active sites and the nucleation rate [33,34].

Scanning electrochemical cell microscopy limits the deposition surface to the diameter of a nanopipette, from a few microns to tens of nanometers. By combining scanning electrochemical cell microscopy with CCTGs and (S)TEM analysis, the electrochemical response of a limited number of clusters and atomic-scale microscopical observations can be directly linked [56]. In this way, the deposition of Ag [47] and Pd [52] evidences that, in addition to the nonclassical growth pathways described previously, the growth centers may be disconnected completely from the surface because of a low adhesion energy (Figure 3a).

Compared with the description of multiple nucleation, the theoretical formulation of the nucleation and growth of a single nucleus is much more simple and accessible to analytical formulations [60] and numerical modeling [35,36]. One way to address this experimentally consists in using nanoelectrodes [60]. By limiting the size of the electrode, it is possible to form, in principle, one nucleus that grows independently. By comparing the CTTs with a one-nucleus growth model, kinetic and mechanistic information on the electrodeposition process can be obtained (Figure 3b). The experimental data using nanoelectrodes ($r \sim 1\ nm$) are in perfect agreement with theoretical predictions. Not surprisingly, the induction time, t_{IND}, becomes longer for smaller electrodes (up to $\sim 10\ s$), reflecting the stochastic nature of

nucleation: the probability of a nucleation event is small and proportional to the area of the electrode.

More recent studies involve the nucleation and growth of single silver clusters on platinum nanoelectrodes evaluated by in situ atomic force microscopy (AFM) [57]. The dependence of t_{IND} on concentration, overpotential, and electrode size is investigated. Much shorter t_{IND} (down to $\sim ms$) are reported. In addition, the existence of latent nucleation sites is confirmed, since repeated deposition experiments show the growth of 1 or 2 single particles at identical locations, within the limitation of AFM ($\sim 10\ nm$). A similar study indicates that, for high overpotentials, the density of active sites may be much higher than that previously thought [61]. The existence of active sites with different activities may be a plausible explanation. These studies also support the hypothesis that the values of J_{ST} and N_0 obtained from multiple nucleation studies at macroelectrodes may reflect nanocluster surface movement and aggregation [19,21].

More recently, the electrochemistry of single entities has demonstrated to be viable on single atoms. Based on the concept of catalytic amplification [62,63], the nucleation of single Pt clusters is measured indirectly through the electrocatalytic reduction of protons in just-nucleated Pt clusters on a carbon ultramicroelectrode (UME) (Figure 3c) [64]. Key to this method is the use of such low concentrations so that even the first event of the nucleation and growth process (discharge of a single Pt ion) is limited by the diffusion rate of ions to the electrode. By using a Bi UME, Zhou et al [65] report the ability of depositing and electrochemically characterizing Pt clusters, atom-by-atom, from a 1-atom to a 9-atom cluster [58] or up to a NP of a few nanometers. These atom-by-atom deposition studies confirm that, whereas 1-atom clusters are stable (not desorbing from the Bi surface), the stepwise addition of more atoms results into only one growing cluster, probably driven by surface area minimization [12,53,54].

Studies reporting nucleation and growth of single entities have been rapidly increasing in the past few years (Figure 3d). Different variants consist in (1) nucleating a single NP on a tunneling UME [66], a confined nanopore [67] or a nanodisk [68] or (2) confining metal salt precursors to either micelles [69] or attoliter water nanodroplets dispersed on an organic solvent [59].

Conclusions

A review of the recent progress in the understanding of electrochemical nucleation and growth of metals on low-energy substrates presents the following scenario. Although theoretical formulations for multiple nucleation are constantly improving, they are not yet

Figure 3
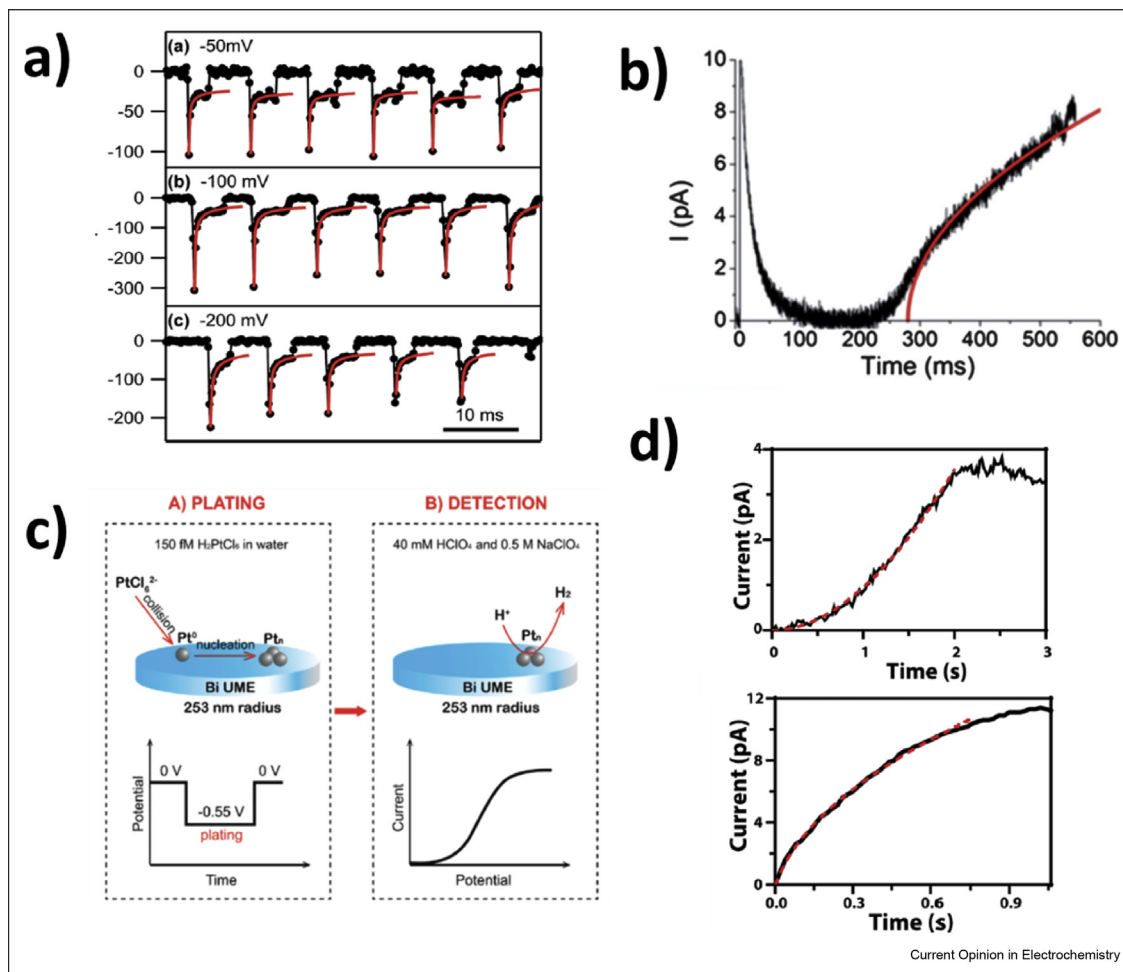
Electrochemical nucleation and growth of single entities. **(a)** Experimental CTTs obtained during the deposition of Ag on HOPG by using SECCM with a nanopipette of d ~400 nm. Reprinted with permission from the study by Lai et al [47], copyright 2015, Royal Society of Chemistry. **(b)** The CTT obtained during the growth of a single Ag nucleus on a 20 nm radius Pt UME. Three regions can be distinguished: zero current (induction time); growth limited by kinetics owing to the small size of the cluster ($I \propto t^2$); and growth limited by mass transport ($I \propto t^{0.5}$). Reprinted with permission from the study by Velmurugan [57], copyright 2012, Royal Society of Chemistry. **(c)** Schematic representation of the experimental protocol for an atom-by-atom single platinum cluster deposition and subsequent detection by electrocatalytic amplification by proton reduction. Reprinted with permission from the study by Zhou et al [58], copyright 2017, American Chemical Society. **(d)** Deposition of Pt from attoliter water droplets colliding with a biased electrode: representative CTTs and fits for nucleation and growth under kinetic (top) and diffusion control (bottom). Reprinted with permission from the study by Glasscott et al [59], copyright 2019, American Chemical Society. SECCM, scanning electrochemical cell microscopy; CTTs, current−time transients; UME, ultramicroelectrode; HOPG, highly oriented pyrolytic graphite.

complete. Therefore, one must be careful with the interpretation of CTTs and the determination of nucleation rates [12,33,34]. Recent experimental findings indicate that several aspects still need to be considered further:

- Nonstationary, time- and site-dependent nucleation rates $J(s,t)$.
- Nonclassical growth pathways: surface detachment [47,52], movement, aggregation, and coalescence of small nanoclusters [19−21]; secondary nucleation [49]; cluster transformation into crystalline NPs via

both gain or loss of atoms [24]; nucleation and dissolution events before the formation of stable nuclei [25]; etc.

In addition, some questions remain unanswered [5,12]. Why do we measure a higher number of nuclei than the calculated number of active sites? Why, in most of the cases, a single atom is a cluster of critical size? These questions point to the need of developing new descriptions of the initial steps of the nucleation process. A plausible answer could be grounded on nucleation

being a nonactivated process. Under this assumption, the initial stages of phase formation could simply involve adsorbed atoms, which collapse into larger clusters, driven by minimization of the overall exposed area and, consequently, of the interfacial energy. With a size-dependent surface mobility, small clusters would be highly mobile. Larger clusters would effectively be fixed on the substrate and would grow not only by direct attachment but also by incorporating other clusters ranging from single atoms to a few nanometers. Further discussion on these views can be found in terms of spinodal decomposition [12,53,54] or of an electrochemical aggregative growth mechanism [19–21,37].

Possibilities to delve further into all the possible growth pathways include (a) higher resolution *in situ* EC-(S) TEM studies that resolve small nanoclusters of $d \sim 1\ nm$; (b) minimization of the electrode surface so that the nucleation and growth of single (or a controlled amount of) clusters can be studied under various experimental conditions; (c) the use of nonaqueous electrolytes with smaller nucleation frequencies; and (d) multiscale modeling approaches that can tackle simultaneously multiple classical and non-classical growth pathways and deliver appropriate $N(t)$ and CTTs to be compared with experimental data.

Conflict of interest statement
Nothing declared.

Acknowledgements

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** of outstanding interest

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