Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for "New In situ Description of Electrodepositing Multiple Nucleation Processes under Galvanostatic Stimuli"

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PART 1

The calculation of equation (1), (2) and (3), (4) are shown in reference **[E. Bosco and S. Rangarajan, Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 1982, 134 (2), 225.]**, as follow:

In each case the current passes through a maximum and then approaches the limiting current for diffusion to a planar electrode. The current I$_{max}$ and the time, t$_{max}$, corresponding to the maximum can be evaluated by equating the-first derivative of each I-t relation to zero. Thus, for progressive nucleation,

$$\frac{dI}{dt}=-\frac{at^{-\frac{3}{2}}}{2}+\frac{at^{-\frac{3}{2}}\exp\left(-bt^2\right)}{2}+2abt^{\frac{1}{2}}\exp\left(-bt^2\right) \qquad \text{(S1)}$$

Where $a = zFD^{1/2}C/\pi^{1/2}$ and $b = AN_{\infty}\pi k^{'}D/2$ (S2)

t$_{max}$ is therefore defined by the equation

$$2abt_{max}^{1/2}\exp\left(-bt_{max}^{2}\right)+\frac{1}{2}*at_{max}^{-\frac{3}{2}}\exp\left(-bt_{max}^{2}\right)-\frac{at_{max}^{-\frac{3}{2}}}{2}=0 \qquad \text{(S3)}$$

which can be rearranged to

$$\left(4bt_{max}^{2}+1\right)\exp\left(-bt_{max}^{2}\right)=1 \qquad \text{(S4)}$$

The algebraic solution of this transcendental equation is not known but approximate solutions can be found in a variety of approximant methods. Using Newton's method

$$t_{max}=\left(\frac{4.6733}{AN_{\infty}\pi k^{'}D}\right)^{1/2} \qquad \text{(S5)}$$

and substituting this into eqn(1), the current at the maximum is

$$I_{max}=0.6382zFDc(kN)^{\frac{1}{2}} \qquad \text{(S6)}$$

The product of ($I_{max}^{2}t_{max}$) does not contain the quantities k, k', AN_{∞}, or N and is therefore a convenient diagnostic criterion to determine whether the nucleation process has been arrested or is still progressing. Thus, for progressive nucleation,

$$I_{max}^2 t_{max} = 0.2598(zFc)^2 D \tag{S7}$$

and for instantaneous nucleation,

$$I_{max}^2 t_{max} = 0.1629(zFc)^2 D \tag{S8}$$

More details are given in reference [E. Bosco and S. Rangarajan, Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 1982, **134** (2), 225.].

With the calculation above, it is easily to find that equation (13) and (14) in our work does not contain the quantities k, k', $^{A,}N_m$, or N, too. Though the parameter values change at varying stimuli conditions, it is noteworthy that the nuclear species remain unchanged regardless of instantaneous or progressive nucleation.

PART 2

The composition of gold electroplating solution in manuscript "New In-situ Description of Electrodepositing Multiple Nucleation Process under Galvanostatic Stimuli" is as follow: $NaAuCl_4$ 5g/L, 5,5-dimethylhydantoin 13g/L and $C_6H_8O_7$ 40 g /L, pH=10.

The experimental galvanostatic stimuli are 0.0125A/dm^2, 0.025mA/dm^2, respectively. And potentiostatic stimuli transients were used the same electrolyte explain above, and the experimental potential is -1V vs. SCE.

All electrochemical measurements in manuscript "New In-situ Description of Electrodepositing Multiple Nucleation Process under Galvanostatic Stimuli" were using a three-electrode electrochemical cell on a CHI760D electrochemical workstation. A saturated calomel electrode (SCE) and titanium electrode covered by iridium oxide (the electrode work area was 2×2 cm^2) were used as reference and counter electrodes, respectively. A copper electrode with work size of 2×2 cm^2 is used as work cathode. All electrochemical measurements performed at room temperature 25 °C.

PART 3

In our previous paper **[G. Luo, D. Li, G. Yuan, and N. Li, J. Electrochem. Soc., 2018, 165 (3), D147.]**, a new limited-diffusion thermotical model was developed. The model is based on single hemispherical nucleus process revealed in SH model and Brownian motion explained in MD model. More details can be found in the published paper.

A limited-diffusion model was proposed to explain the deviations, based on single hemispherical nucleation process and Brownian motion, with the consideration that electric field distribution on electrode surface is limited during electrodeposition. The present model also originates from a simple view of the nucleation and growth of individual nuclei, and nuclei random distribution on the electrode surface. In a schematic form, the conception of our model is based on the five assumptions listed below:

(1) Ions with a solvation sphere migrate in the bulk solution described a Brownian motion. Ions which randomly cross a hemispherical surface defined by a radius R, will lose their solvation shells in the hemispherical area as shown in figure 1. The hemispherical surface is regarded as first reaction boundary and the radius *R* is the largest critical distance around a nucleation site for mass transfer

with diffusive motion assisted by an electric field. In present model, the radius *R* is assumed to be constant for a given electrolytic solution during the growth process.

(2) For single nuclei, ions inside the first reaction boundary (region II in figure 1 in figure S1-a), migrate towards an electroactive site by performing a diffusive motion assisted by an electric field. And ions outside the first reaction boundary (region I in figure S1-a), migration is described as Brownian motion.

(3) As the radii of diffusion zone of single nuclei expanded, the diffusion zone transfers from hemispherical to cylindroid on planar electrode because of ions equiprobable discharging at the same distance from electrode surface, as shown in figure S1-b. The height of cylinder is limited to *R* as mentioned in assumption (1). The base area of cylinder is a function of time.

(4) Based on electrical double layer on electrode surface, there is a limited distance of diffusion zone in electrolyte defined by *d*, *d*=*R*, as shown in figure S1-c. Inside the first reaction boundary (region II in figure S1-c), ions migrate towards electrode surface by performing a diffusive motion, while ions migrate describing a Brownian motion outside the boundary.

(5) At the electroactive site, ions are reduced, form a nucleus and growth, initiating thus the deposition process. This model describes a three-dimensional nucleation, and the two-dimensional nucleation is not analyzed.

The assumption (3) is the most likely reason for the deviation of the experimental curves shown in Figure 4 at larger t/t_m. More details are given in original paper [G. Luo, D. Li, G. Yuan, and N. Li, J. Electrochem. Soc., 2018, 165 (3), D147.].

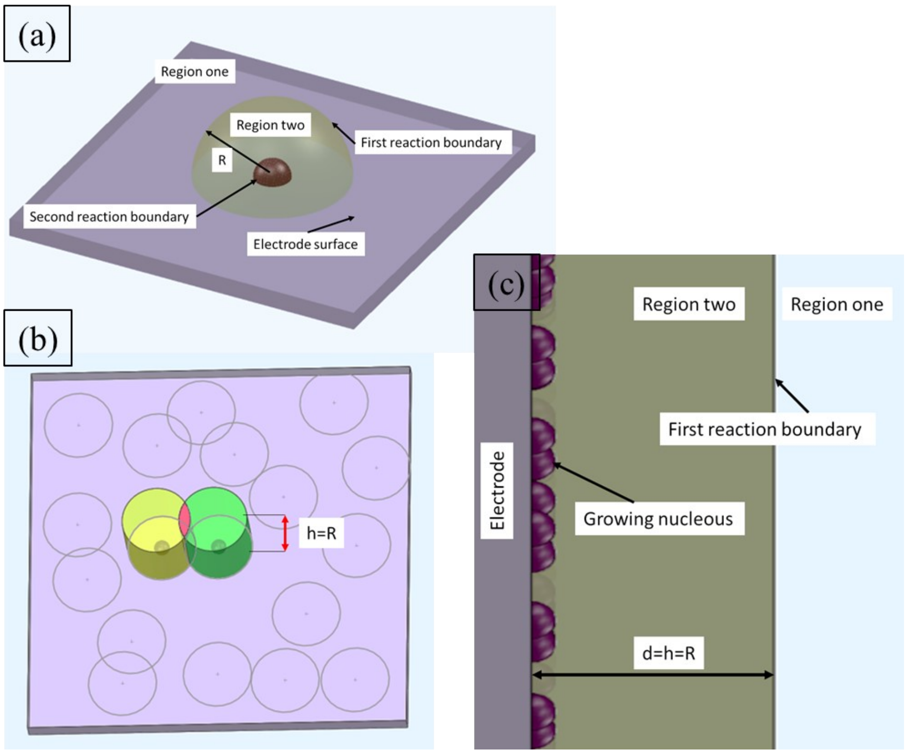

Figure S1 Diagrammatic drawing of diffusion zone transfers from hemispherical to cylindroid on planar electrode; a) the different regions distribution of single nuclei; b) overlap of diffusion zone transfers from hemispherical to cylindroid; c) Schematic representation of the different regions and surfaces of planar electrode

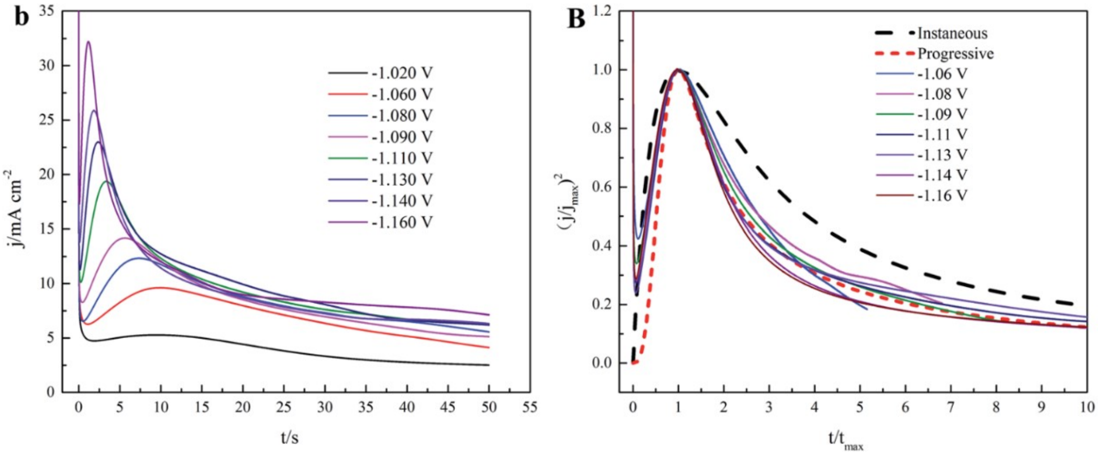

Figure S2 The chronoamperometry at various step potentials and the corresponding dimensionless experimental curves with their theoretical curves for instantaneous and progressive nucleation processes of the GC electrode as cited by **Ref.[J. Zhang, A. Liu, X. Ren, J. Zhang, P. Yang, and M. An, RSC Adv., 2014, 4 (72), 38012.]**

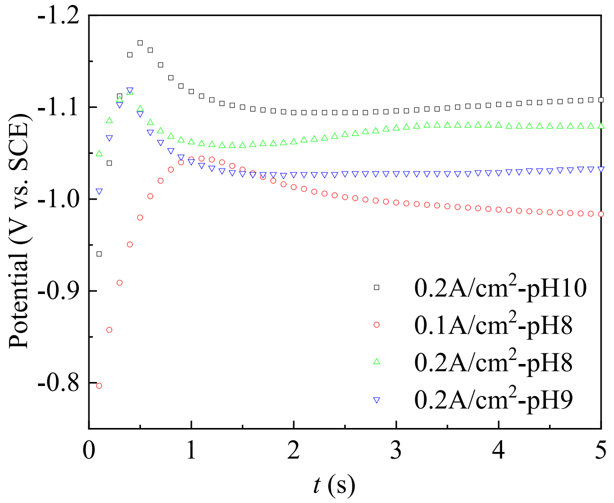

Figure S3 The chronopotentiometry curves at various pH and current density of gold electrodeposition plotted by our experimental data

Table S1 Current transformation equation at diffusion-controlled electrodeposition

Year/Author	Current transformation equation
1983/ B. Scharifker and G. Hills [1]	For instantaneous nucleation: $I = zFcD^{\frac{1}{2}} \Big/ (\pi t)^{\frac{1}{2}}(1 - exp(- N\pi kDt))$; For progressive nucleation: $I = zFcD^{\frac{1}{2}} \Big/ (\pi t)^{\frac{1}{2}}\left(1 - exp\left(- AN_m\pi KDt^2/2\right)\right)$
1984/ B. Scharifker and J. Mostany[2]	Current function formula: $I = \left(\frac{zFD^{\frac{1}{2}}c}{\pi^{\frac{1}{2}}t^{\frac{1}{2}}}\right)\left(1 - \exp\left\{ - N_0\,\pi kD\left[t - \frac{1 - e^{-At}}{A}\right]\right\}\right)$ For instantaneous nucleation: $\alpha \to 0$: $I = \left(\frac{a}{t^{\frac{1}{2}}}\right)[1 - \exp(- bt)]$; For progressive nucleation: $\alpha \to \infty$: $I = \left(\frac{a}{t^{\frac{1}{2}}}\right)[1 - exp(- Abt^2)]$
1987/ M. Sluyters-Rehbach et al.[3]	Current function formula:

	$I(t) = \frac{1}{\alpha(At)^{\frac{1}{2}}}(1 - exp[-\alpha(At)^{\frac{1}{2}}\{(At)^{\frac{1}{2}} - e^{-At}\int_0^{(At)^{1/2}} e^{\lambda^2} d\lambda\}$; Current equation: $t^{-1/2}\ln\left[1 - \frac{(\pi t)^{1/2} j(t)}{zFcD^{1/2}}\right] = -\theta_{ex} t^{-1/2} = \alpha A^{1/2}\left\{(At)^{1/2} - e^{-At}\int_0^{(At)^{1/2}} e^{\lambda^2} d\lambda\right\}$ Current function formula:
1999/ L. Heerman and A. Tarallo[4]	$j(t) = zFDc(\pi Dt)^{\frac{1}{2}}\frac{\Theta}{\emptyset}(1 - \exp[-\alpha N_0(\pi Dt)^{\frac{1}{2}}t^{\frac{1}{2}}\Theta])$; For instantaneous nucleation:: $\bar{\delta}(t) = (\pi Dt)^{\frac{1}{2}}$; For progressive nucleation:: $\bar{\delta} = (3/4)(\pi Dt)^{\frac{1}{2}}$
1999/ D'Ajello PCT and Munford ML[5]	For instantaneous nucleation: $j = 2\pi NDRzFc_0 b\left(1 + \frac{RN^{1/2}}{\sqrt{at}}\right)[1 - exp(-at)]$; For progressive nucleation: $j = 2\pi N_\infty DRzFc_0 b\left(1 + \frac{\sqrt{2}\,R\sqrt{AN_\infty}}{\sqrt{a^{'}t}}\right)\left[1 - exp\left(-a^{'}t^2\right)\right]$
2006/ M.Y. Abyaneh[6]	Cone model: $(j)_{R.C.C.} = \frac{zF\rho}{M}\tan\alpha\frac{dR_0}{dt}[1 - exp(-\pi R_0^2 N_0)]$; Hemispherical model: $(j)_{Hemi} = 2\frac{zF\rho}{M}\frac{dR_0}{dt}\tau exp(-\tau^2)\int_0^\tau exp(s^2)ds$
2018/ Vladimir A. Isaev, O.V. rishenkova [7]	For instantaneous nucleation: $j = 2\frac{ze}{v}k_1 x\omega(x) = 2\frac{ze}{v}k_1 xexp(-x^2)\int_0^x exp\xi^2 d\xi$ For progressive nucleation: $j = 3\frac{ze}{v}k_1\omega_2(y) = 3\frac{ze}{v}k_1 exp(-y^3)\int_0^y (y^2 - \xi^2)exp(3\xi^2 - 2\xi^3)d\xi$
2018/ Luo G., Li D. Y., Yuan G. H., Li N. [8]	For instantaneous nucleation: $I = zFc_0 D^{\frac{1}{2}}\Big/\pi^{\frac{1}{2}}\left(\frac{\sqrt{\pi D}}{R} + \frac{1}{\sqrt{t}}\right)(1 - \exp(-N\pi kDt))$;

For progressive nucleation:

$$I = zFc_0 \, {}^{D^{\frac{1}{2}}}\Big/_{\pi^{\frac{1}{2}}} \left(\frac{\sqrt{\pi D}}{R} + \frac{1}{\sqrt{t}}\right)\left(1 - \exp\left(-AN_m \pi k' D^{t^2}\big/_{2}\right)\right)$$

References

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7. V. A. Isaev, O. V. Grishenkova and Y. P. Zaykov, *Journal of Electroanalytical Chemistry*, 2018, **818**, 265-269.
8. G. Luo, D. Y. Li, G. H. Yuan and N. Li, *Journal of the Electrochemical Society*, 2018, **165**, D147-D151.

Table S2 The electrocrystallization parameters of Ag deposition on GCE under different stepped potentials as cited by Ref. [Huang, S. S., Liu, C., Lin, L., Yang, F. Z., Tian, Z. Q. *Journal of Electrochemistry*. 2018, **24**(04): 344.]

E（$vs.$ SCE）(mV)	$10^3 I_m$ (A·cm^{-2})	t_m (s)	$10^6 I_m^2 t_m$ (A^2·s·cm^{-4})	$10^6 D$ (cm^2·s^{-1})	$10^{-5} N_0$ (cm^{-2})
-750	-20.9	0.790	344	7.27	3.26
-765	-28.9	0.412	344	7.28	6.25
-780	-30.7	0.375	354	7.48	6.68
-795	-34.4	0.310	366	7.74	7.80
-810	-38.4	0.250	340	7.61	9.85
-825	-40.5	0.230	376	7.95	10.2