

Morphology of Nanostructured Films Synthesized via Electrodeposition

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ABSTRACT

In this study we perform Brownian dynamics simulations to investigate the influence of surface reaction rate on the development of size dispersion of interfacial nanostructures that form by electrodeposition of non-interacting ions (particles) onto surfaces with randomly distributed nucleation sites. The surface reaction rate is incorporated into the simulations by using a reaction probability that approaches unity in the case of instantaneous, diffusion-limited deposition. It is found that the size uniformity of the growing particles on the randomly distributed active sites can be improved by decreasing the reaction probability. The simulation results, in qualitative agreement with experiments, show that decreasing the reaction probability is an effective means to weaken the interparticle diffusion coupling by reducing the overlap of diffusion zones surrounding the nanoparticles, and thereby reduce the particle size dispersion.

Keywords: Brownian dynamics, nanostructured films, electrodeposition, morphology, size dispersion

1 INTRODUCTION

In recent times, there has been a growing interest in micro and nanostructured interfaces due to their importance in diverse applications. Examples of interfacial nanostructures include functional coatings and thin films, sessile bacterial colonies on physiological surfaces and, metal semiconductor nanoensembles. There is an interest in carefully designing deposition processes for the manufacture of novel optical and electronic devices with controlled nanostructures. Hence a central issue in the synthesis of interfacial nanostructures is the control of the morphology of the interface.

The size dispersion of growing ensembles is used to characterize the morphology of interfacial structures that are formed by the irreversible deposition of particles or molecules from a bulk solution phase. The arrangement of nucleation sites on the surface have been shown to influence the development of size dispersion during the deposition process. For instance, in the case of non-interacting metal ions that nucleate instantaneously, previous Brownian Dynamics simulation (BDS) for diffusion-controlled growth of metal nanoparticles on

planar surfaces [1] has shown that particle size dispersion of metal nano-ensembles develops when active (nucleation) sites are randomly positioned on the electrode surface. The particles become more size-similar with increasing deposition time provided that active sites are regularly arranged. Therefore, size uniformity can be accomplished by distributing the active sites regularly on the electrode surface.

However, in several systems of practical interest, the distribution of active sites is random and the size dispersion develops very quickly with increasing deposition time if the particles nucleate instantaneously and the process is diffusion controlled. Therefore, in order to obtain uniform nanostructures, it is important to seek strategies to control the particle size dispersion for such systems. One of the techniques to reduce size dispersion is to “slow-down” the rate of growth, as demonstrated experimentally in the potentiostatic double-pulse electrodeposition of silver ions. In these experiments, a short initial pulse at a high overpotential is used to initiate the formation of the nuclei, and a longer second pulse at lower overpotential is used to control the growth of the nuclei. Penner [2] demonstrated the benefits of slow growth for double pulse experiments by performing BDS for electrodeposition of metal ions on electrode surfaces. In his simulation, Penner considered an ensemble of nuclei initially grown in the diffusion-controlled regime. He further considered a Nernst layer on the electrode surface, so that changing the overpotential could vary the concentration of ions on the electrode surface, and smaller overpotentials lead to slower growth, thereby reducing size dispersion.

In this paper, we investigate the influence of the surface reaction on the morphology of nanostructures formed by electrodeposition. We present a generic framework to incorporate a finite reaction rate between the free particle and the nucleation site. We also present the results of 3-dimensional BDS for the influence of surface reaction rate on the development of size dispersion of interfacial structures. The balance of the surface reaction rate to the bulk diffusion rate is incorporated into the BDS by using a stochastic reaction probability that approaches unity in the case of diffusion-limited growth [3-5]. For surface-bound electrodeposition, it is anticipated that the reaction probability, can be reduced by decreasing the current density or by changing the electrolyte properties [3].

2 SIMULATION TECHNIQUE

In the BDS we keep track of the coordinates of a set of spherical particles for a dilute system based on the numerical solution of the Langevin equation that represents the force balance for each particle i . The particle trajectory can be computed according to [6]

$$r_i(t + \Delta t) = r_i(t) + \frac{D}{\kappa T} F_E(t) \Delta t + \Delta r^g \quad (1)$$

where $r(t+\Delta t)$ is the position vector of the center of the particle at time $t+\Delta t$, F_E is the resultant force vector due to all external forces acting on the particle, and Δr^g is the Brownian random displacement due to diffusivity D of the particle and is chosen independently from a Gaussian distribution with zero mean and variance equal to $2D\Delta t$.

The influence of the electric field on the transport of charged species (electromigration) is neglected, thereby assuming that the concentration of the supporting (inert) electrolyte is high [7]. We further assume quiescent conditions i.e. we neglect forced and natural convection. The particles (ions) are assumed to be diffusing Brownian objects and the particle trajectories are given by

$$r_i(t + \Delta t) = r_i(t) + g_q(\sqrt{2D\Delta t}) \quad (2)$$

where g_q is a vector of Gaussian distributed random numbers with zero mean and variance of unity. We define dimensionless space and time variables as

$$\bar{r}_i = r_i / a, \quad \bar{t} = Dt / a^2 \quad (3)$$

where a is the particle radius. Then, Eq. 2 is simplified as

$$\bar{r}_i(\bar{t} + \Delta \bar{t}) = \bar{r}_i(\bar{t}) + g_q \sqrt{2\Delta \bar{t}} \quad (4)$$

The boundary condition at the interface is derived from a balance between diffusion and reaction at the surface. In this study we consider an irreversible first-order surface reaction with lumped surface kinetic rate, k_c . In dimensional form

$$k_c C_{r=R} = D \left. \frac{\partial C}{\partial r} \right|_{r=R} \quad (5)$$

where, C is the particle concentration and r is the radial distance measured from the center of the nucleus of radius R . Such a mixed (Robin-type) boundary condition on the surface has been used to model electrochemical processes in which ions of the depositing species diffuse to the surface, and are discharged and deposited at the surface [8]. Eq. 5 can be expressed in dimensionless form, as Eq. 6, using the scales introduced in Eq. 3 and $C=C_b$, where C_b is the bulk concentration [3,5] as

$$(1 - P_s) \left. \frac{\partial \bar{C}}{\partial \bar{r}} \right|_{\bar{r}=\bar{R}} - P_s \bar{C} \Big|_{\bar{r}=\bar{R}} = 0 \quad (6)$$

where the reaction probability, P_s , represents the relative ratio of the kinetic rate of attachment to the rate of diffusion from bulk to the surface, i.e.,

$$P_s = \frac{Da}{1 + Da} \quad (7)$$

where Da is a Damkohler number defined as $Da=k_c a/D$. P_s is interpreted as the probability of reaction to take place once a free particle reaches the interface. The limit $P_s \rightarrow 1$ denotes growth limited by the diffusion of the particles from the bulk to the surface, and $P_s \ll 1$ indicates that the whole process is controlled by the reaction at the surface.

The reaction probability is dependent on the deposition overpotential, limiting current, exchange current and bulk electrolyte concentration. Voss and Tomkiewicz [9] showed that P_s can be related to the electrochemical parameters as

$$\frac{1}{P_s} = \frac{f_c(\eta) + f_a(\eta)}{f_c(\eta) - f_a(\eta)} + \frac{I_L / I_0}{f_c(\eta) - f_a(\eta)} \quad (8)$$

where

$f_c(\eta) = \exp(\alpha_c F \eta / RT)$; $f_a(\eta) = \exp(\alpha_a F \eta / RT)$ and I_0 is the exchange current, I_L is the limiting current, α_c and α_a are the charge transfer coefficients for the cathodic and anodic reactions, η is the deposition overpotential, F is the Faraday number, R is the gas constant and T is the temperature.

The simulations for nanoparticle growth are performed in three dimensional simulation boxes with periodic boundary condition in the x and y directions. At the beginning of the simulation, active (nucleation) sites are randomly distributed on the deposition surface, and the number of these active sites is kept constant during the course of the simulation. The initial system corresponds to an isothermal, monodispersed homogenous system with particle concentration equal to bulk electrolyte concentration. The motion of particles are simulated according to Eq. 4. In the course of the simulation, when the free particles come into contact with any of the active sites on the surface they will attach on it with a finite reaction probability P_s [5]. Once the particle has reacted with the nucleus, the radius of the hemispherical nucleus is increased in such a way that the volume of the hemispherical nucleus is increased by an amount equal to the volume of the free particle. This is done so that the growth of the nuclei is consistent with the Volmer-Weber growth mechanism as observed experimentally for the deposition of silver ions on low surface energy surfaces [10].

3 RESULTS AND DISCUSSIONS

In order to investigate the temporal evolution of the particle size dispersity, the standard deviation of the radii of the growing nanoparticles on the deposition surface, $\sigma(t)$, is used as a quantitative measure. Figure 1 shows the temporal evolution of the particle size dispersion for four different values of reaction probability, ranging from 0.2 to 1.0. Error bars shown in the results indicate one standard deviation of the result that was calculated for the four simulations performed using different seeds on the random number generator. The evolution of the standard deviation with time has similar qualitative trends irrespective of the value of P_s . The size dispersion initially increases rapidly

for short times. This is followed by a time period until $t=t_c$ in Figure 1 during which the standard deviation decreases or remains practically unchanged. For $t>t_c$, σ increases with increasing time. However, differences exist among the evolution of σ for different P_s values. Specifically, the long-time evolution of the standard deviation changes from a slow increase for $P_s=0.2$ to a rapid increase for $P_s=1$. As shown in the inset in Figure 1, the slope of the linear best fit of σ vs. t curve at long times, S_σ , increases with reaction probability P_s .

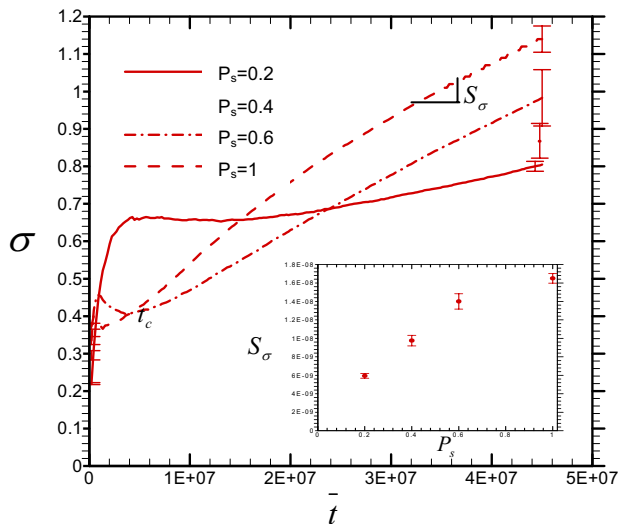


Figure 1: Standard deviation of the particle radius, $\sigma(t)$, as a function of time for different reaction probabilities, P_s . Inset shows slope S_σ of standard deviation versus time plots at different values of P_s .

We further investigated whether the density of active sites could influence the behavior of the σ vs. t curves by performing simulations for lower nucleation densities. These simulation results (not reported here) showed that the influence of P_s on σ is qualitatively independent of nucleation density. However it was observed that for a given P_s , σ is lower for the surface with lower nucleation density. This implies that the size monodispersity of particles can be improved by decreasing the nucleation density on the surface. This result is consistent with experiments in which the relative size monodispersity of particles was found to improve by lowering nucleation density via decreasing the overpotential of the growth pulse [11].

The relative size dispersity (RSD) of the growing nanoparticles (characterized by the ratio of the standard deviation to the mean radius) is shown in Figure 2. At long deposition times, the RSD remains nearly constant at low values of P_s and increases with time for larger P_s . Moreover, as shown in the inset in Figure 2, the slope of the linear best fit of RSD vs. time curve at long times, increases

rapidly as the P_s increases. This observation leads to the conclusion that a strategy to improve the size uniformity of particles growing on a random distribution of nucleating sites on a deposition surface would be to reduce the reaction probability P_s and thereby slow the growth of the nanoensembles.

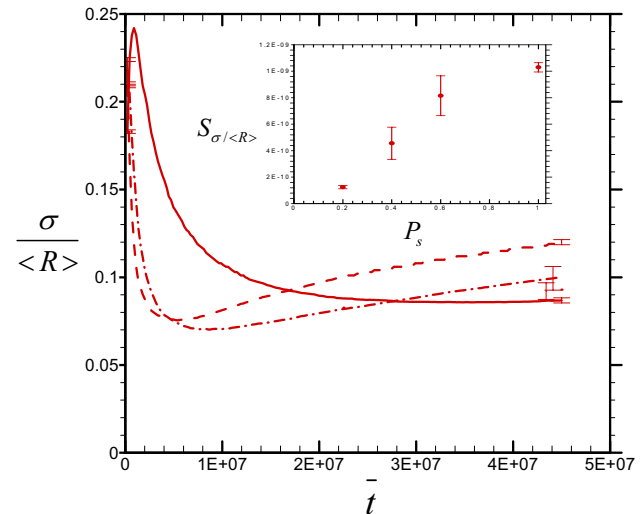


Figure 2: Relative size dispersity of the particle radius, RSD, as a function of time (legend same as in Figure 1). Inset shows slope of relative standard deviation versus time plots at different values of P_s .

The influence of P_s on the size dispersion of the growing nanoparticles can be explained by the dependence of the growth of the nanoparticles on a surface to the distance of the particle to its nearest neighbor, NND from here onwards. A previous study of diffusion-limited growth of nanoparticle ensembles randomly distributed on deposition surface showed an increase in the growth of nearest neighbors as the proximity between the particles increased [1]. This phenomenon of retardation in growth of densely nucleated regions has been referred to as interparticle diffusional coupling [1,2]. In our simulations we investigate the effect of P_s on interparticle diffusional coupling. Towards this end, we compute the increase in the radii of each nucleation site, $\Delta r = r(t) - a$, normalized with respect to the corresponding ensemble averaged value, $\langle \Delta r \rangle$ for different times. Figure 3 show results from a single simulation of $\Delta r / \langle \Delta r \rangle$, as a function of NND obtained for $P_s = 0.2$ and $P_s = 1$. It can be seen from these figures that there exists a stronger linear correlation between growth of particles and the NND for $P_s = 1$ as compared to that observed for $P_s = 0.2$. Simulations at other values of P_s support the conclusion that lower values of P_s lead to a reduced correlation between particle radii and NND, and hence result in an improvement in the size uniformity of growing nanoparticles. The simulations at lower nucleation density had a reduced linear correlation between particle radii and NND as compared to the higher nucleation density.

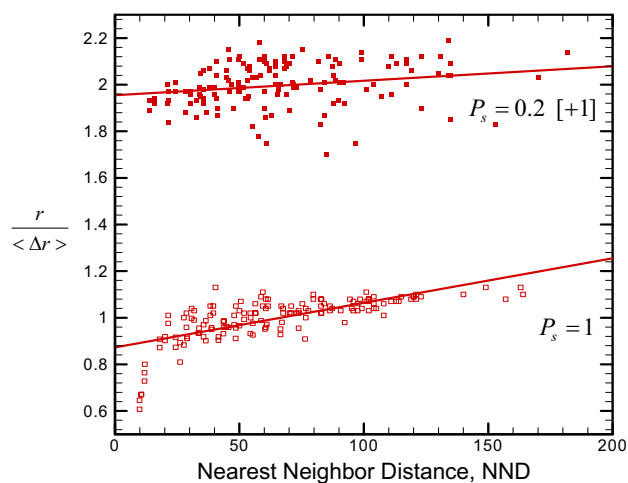


Figure 3: Particle growth, $r / \langle \Delta r \rangle$, versus the nearest neighbor distance for one simulation performed at $P_s = 0.2$ and $P_s = 1.0$. Results for $P_s = 0.2$ have been incremented by one unit for clarity.

4 SUMMARY

In this paper, the influence of the surface reaction rate on the morphology of interfacial nanostructures is discussed. A reaction probability P_s was introduced into the simulations, to account for the different modes of growth, ranging from diffusion controlled at $P_s = 1$ to surface reaction controlled for $P_s \ll 1$. For the growth of metallic nanoparticles on a surface, it was shown that a strategy for improving the size uniformity of nanoparticles is to reduce the reaction probability, and therefore slow the surface reactions. Lower reaction probability reduce the competition between nearest neighbors, leading to a reduction in particle size dispersion. These results can be used to potentially design deposition processes to create interfacial nanostructures with tailor-made morphology. This can be accomplished by manipulating the process variables that effect P_s by controlling the surface reaction rate (via the applied current density) and/or the bulk diffusivity.

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