Early Stages of Electrochemical Nucleation and Growth on Carbon Substrates: Nanocluster Aggregation, Coalescence and Recrystallization

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Metal nanocrystals are of great interest due to their unique properties which differ from their bulk counterparts and can be tuned by adjusting their size and shape. When supported on different substrates, they represent the cornerstone for numerous applications in different fields, such as catalysis or sensing. Electrochemical deposition allows the growth of the nanostructures in one step, directly on the final support. Hence, it has been proven effective to obtain highly electroactive nanostructures with potential for fuel cell or (bio)sensing applications.

One of the key issues to benefit from their properties is to understand their formation mechanisms to achieve a good control of their morphology. However, the early stages of nucleation and growth are still an active field of research and remain unraveled. The classical theory predicts that nanocrystals grow irreversibly by atomic addition until the reaction is halted. However, recent work in colloidal synthesis has indicated that small nanoparticles grow by aggregation and coalescence to a bigger extent than by atomic incorporation. However, electrochemical deposition and thin film growth in general have always been studied considering atomic incorporation as the only growth mechanism.

In this work, we combine Field Emission Scanning Electron Microscopy (FESEM), aberration-corrected Transmission Electron Microscopy (TEM), electron tomography and electrochemical characterization to study the early stages of metal electrodeposition onto carbon substrates. We use carbon coated TEM grids as electrochemical electrodes so that atomic scale characterization can be directly linked with electrochemical measurements[1].

During the analysis of silver and platinum electrodeposition, we observe several phenomena which contradict the classical theories of electrochemical nucleation and growth.
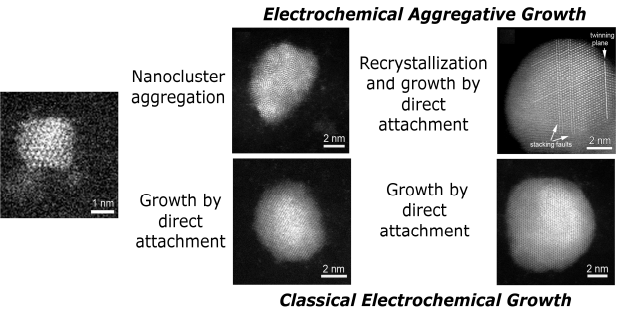

Figure 1. Silver: growth by nanocluster aggregation and coalescence, and by direct attachment[2].

In the case of Ag electrodeposition, it has been found that large clusters (d≥6 nm) grow in number and size with time according to conventional electrochemical nucleation and growth models, whereas small clusters (d≈1-2 nm) do not grow and diminish in number after a certain deposition time. In addition, structural characterization by means of HR-(S)TEM has confirmed that the early stages of Ag electrodeposition are driven by nanocluster surface diffusion, aggregation, coalescence and recrystallization[2] (fig. 1).

In the case of Pt electrodeposition, similar phenomena have been found. In addition, by means of electron tomography and HR-(S)TEM, it is shown that dendritic nanostructures with different degrees of porosity are formed at deposition at different potentials. It is confirmed that these nanostructures have been formed by the aggregation and partial coalescence of size-monodispersed nanoclusters of d ≈ 2±1 nm. The degree to which Pt nanostructures coalesce and recrystallize is dependent on the deposition potential and drives the resulting morphology.

To explain the observed phenomena, we propose a reformulation of the Volmer-Weber 3D island growth mechanism. We develop an Electrochemical Aggregative Growth Mechanism which mimics the atomistic processes during the early stages of thin-film growth, by incorporating nanoclusters as building blocks. We show that the early stages of electrodeposition are driven by nanocluster self-limiting growth, surface movement and aggregation. Later growth stages are driven by the extent of nanocluster coalescence and recrystallization[3] (fig. 2).
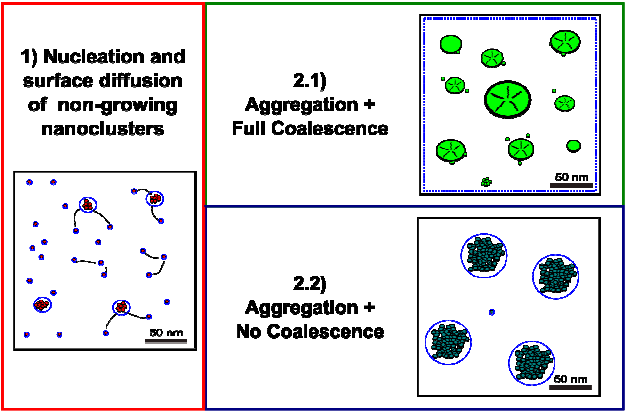

Figure 2. Electrochemical growth by nanocluster aggregation, coalescence and recrystallization.

We discuss the influence of these key phenomena on the growth mechanisms, on the morphology of the resulting nanostructures, and on the interpretation of potentiostatic current transients. The mechanism we propose represents a scientific breakthrough from the fundamental point of view. It also indicates that achieving the right balance between nucleation, self-limiting growth, cluster surface diffusion, and coalescence, is essential for electrochemical deposition processes.

(1)   Ustarroz, J.; Gupta, U.; Hubin, A.; Bals, S.; Terryn, H. *Electrochem. Commun.* **2010**, *12*, 1706–1709.

(2)   Ustarroz, J.; Ke, X.; Hubin, A.; Bals, S.; Terryn, H. *J. Phys. Chem. C* **2012**, *116*, 2322–2329.

(3)   Ustarroz, J.; Hammons, J. A.; Altantzis, T.; Hubin, A.; Bals, S.; Terryn, H. *Manuscript submitted for publication, JACS* **2013**.