Electrodeposition at Nanoelectrodes

by Jeyavel Velmurugan

Major differences can be expected between nucleation/growth processes occurring on nanoelectrodes and on micrometer-sized electrodes. The reported values of the active site density on metal surfaces (N_0) are in the range $10^4 < N_0 < 10^{10}$ cm^{-2},[1] and typically N_0 does not exceed ~10^8 cm^{-2}. Thus, the expected number of active sites on the surface of a ~30-nm-radius electrode is <<1. Our research is aimed at investigating the feasibility and mechanism of electrodeposition of metals at nanoelectrodes.

The electrodes were prepared by heat sealing/pulling an annealed 25 μm Pt wire into a borosilicate capillary under vacuum with the help of a laser pipet puller.[2] We have recently developed methodology for quantitative control of the amount and the shape of the deposited metal.[3]

Electrodeposition of a liquid metal (Hg) at Pt nanoelectrodes was used as a model system because Hg surface is uniform, and defect-free; its growth is not accompanied by the formation of dendrites and other complications. In Fig. 1, a Pt disk radius (a = 69 nm) was determined from the steady-state voltammogram of 2 mm $Ru(NH_3)_6^{3+}$ obtained before deposition of mercury. Mercury was deposited at this electrode by stepping its potential to -100 mV vs Ag/AgCl for 3.5s (calculated time required to form a 69-nm-radius Hg hemisphere). Thus, the shape of deposited Hg was expected to nearly hemispherical with the effective radius close to 69 nm. The ratio of the limiting currents of $Ru(NH_3)_6^{3+}$ 1.5 is in good agreement with the theoretical prediction ($i_{hemisphere}/i_{disk} = 2\pi/4 = 1.57$ [4]).

The results indicate that Hg can be electrodeposited at nanoelectrodes of this size with two possibilities: either an Hg droplet still nucleates in the absence of an active site, or it starts growing on the entire surface of the nanodisk forming a spherical cap. A simple theory assuming diffusion-controlled quasi-steady-state growth (i.e., steady-state diffusion to the growing Hg surface) was developed for these two cases.[4] The main difference between the two dimensionless current–time working curves is that the initial current value for the growing nucleus is close to zero, while in the spherical cap model it is equal to the diffusion limiting current of Hg_2^{2+} to the nanodisk
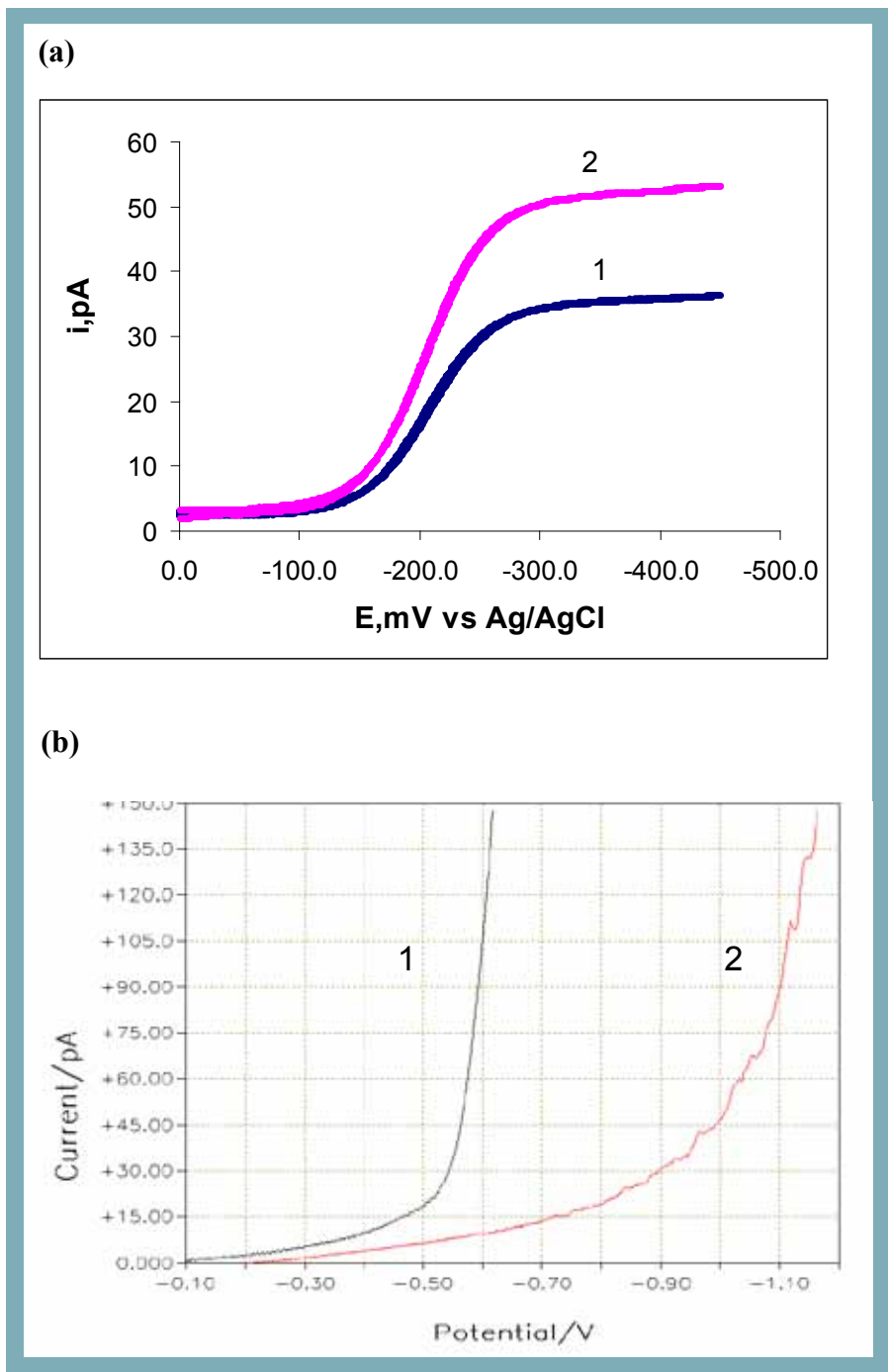
(a)

(b)

Fig. 1. *Voltammograms obtained in 2 mM $Ru(NH_3)_6Cl_3$ (A) and 0.01 M HNO_3 (B) solutions before (1) and after (2) the electrodeposition of a Hg hemisphere on the surface of a Pt nanoelectrode.[2]*

surface. Figure 2 shows an example of two different growth mechanisms of Hg at a Pt nanoelectrode at different over potentials. The adjustable parameter used to fit the data to the theory is the electrode radius.

The study of the formation and growth of single Hg nuclei should yield answers to fundamental questions about the initial steps of electrocrystallization at nanoelectrodes. For example, what is the rate-limiting step of this process? It was recently suggested that the kinetics of the early stage electrodeposition at macroscopic electrodes is controlled by surface diffusion and adsorption.[6] In contrast, at a nanoelectrode, the surface diffusion control is possible only on the extremely short time scale (i.e., µs). Using the developed methodology, it should be possible to prepare 5-10 nm-radius electrodes and study the catalytic properties of such clusters.

About the Author

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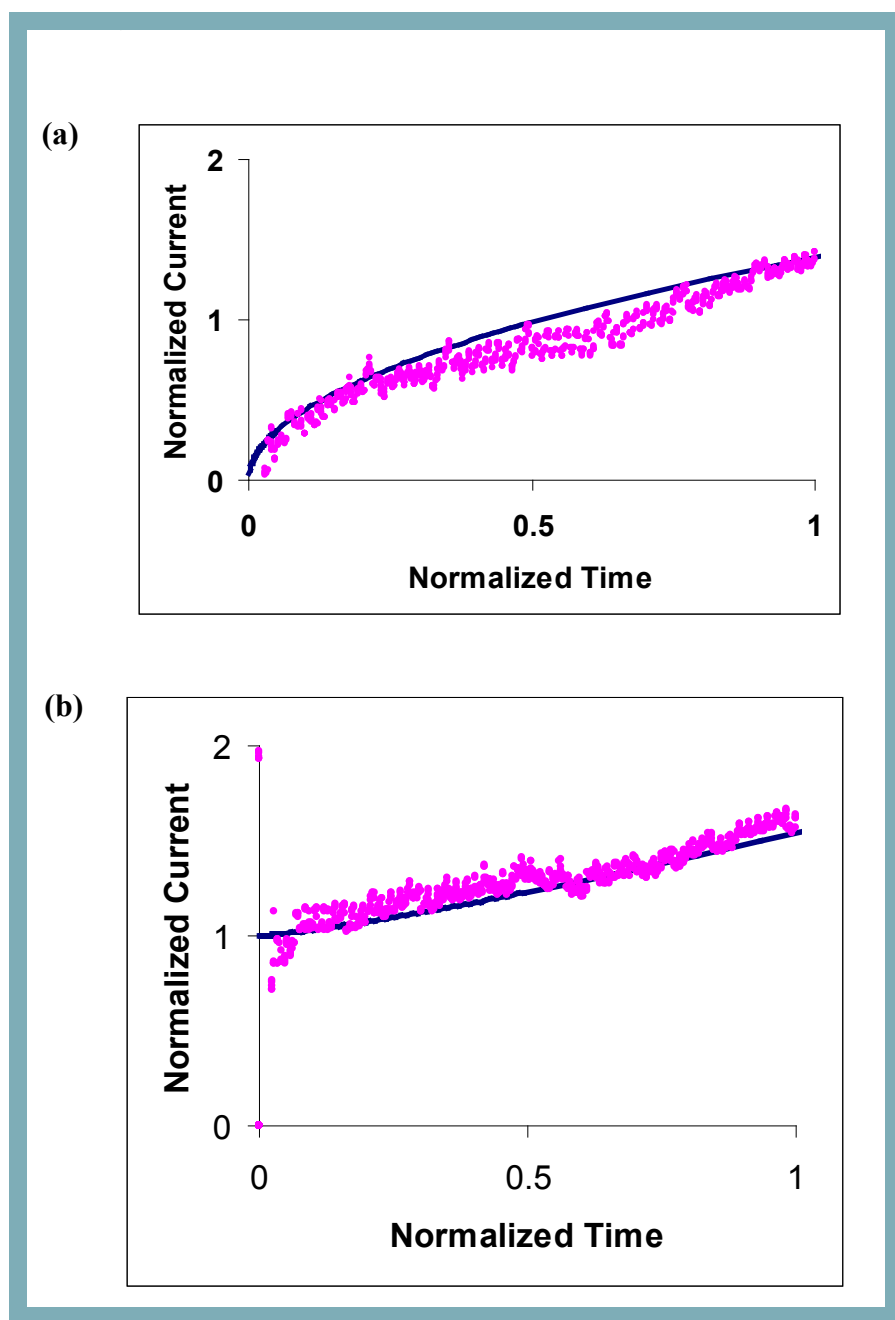6. A. Radisic, P. M. Vereecken, J. B. Hannon, P. C. Searson, and F. M. Ross, *Nano Lett., **6**, 238 (2006).

Fig. 2. *Theoretical (blue) and experimental (pink) current–time curves for a growing hemispherical nucleus (A) and a spherical cap (B) obtained at 60 nm radius Pt electrode in 100 µM of Hg$_2$(NO$_3$)$_2$ and 0.1M HNO$_3$. The potential is stepped to -50mV and -200mV vs Hg quasi-reference in A and B respectively.[5]*