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Nucleation and growth mechanism for the electropolymerization of aniline on highly oriented pyrolytic graphite at higher potentials

Received: 15 May 2000 / Accepted: 6 June 2000 / Published online: 1 March 2001
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Abstract In this work, the nucleation and growth mechanism for the electropolymerization of aniline was investigated at higher potentials on highly oriented pyrolytic graphite by potentiostatic current-time transient and atomic force microscopic (AFM) measurements. The electrochemical data fitted to the theoretical curves for the nucleation and growth suggest that electropolymerization of aniline follows the three-dimensional growth and progressive nucleation mechanism. These results were also compared with the results obtained at lower potentials. The results obtained from transient analysis, at higher potentials, were in good agreement with the results of AFM images.

Key words Nucleation · Growth · Polyaniline · Graphite

Introduction

Studies on electrochemical and surface properties of conducting polymers, particularly those related to polyaniline, polypyrrole and polythiophene, have received considerable attention in the last few years. A wide variety of conducting polymers can be used as charge storage materials [1, 2, 3], electrochromic materials [4, 5], sensors [6, 7], semiconductor photoelectrode coatings [8] and microelectronic devices [9, 10]. The kinetics and geometry as well as the electrochemical responses for the electropolymerization of polymers are highly dependent on the surface properties. Hence, as far as applications are concerned, the role of surface morphology is very important.

Under particular conditions, the mechanism for the nucleation and growth of conducting polymers was found to be three-dimensional (3-D) instantaneous [11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21]. In all these studies it was reported that the electropolymerization of aniline includes a nucleation process similar to the nucleation process at metal deposition, and that polyaniline growth obeys two-dimensional (2-D) progressive nucleation [22]. Moreover, 3-D progressive and 2-D progressive nucleation have been reported in sulfuric acid and perchloric acid media, respectively [23].

To date, as far as conducting polymers are concerned, the predictions for nucleation and growth mechanisms have been mostly made using the results obtained from potentiostatic current-time transient measurements. However, it is necessary to verify the mechanism by some other suitable technique. To this end, AFM is found to be an effective tool to observe the changes in the surface morphology of conducting polymers [24, 25]. In addition, mostly gold and platinum electrodes have been used to study the nucleation and growth mechanism [22, 26]. However, to observe the molecular structure of nucleation by AFM, it is better to choose a flat surface substrate for atomic resolution. In addition, it is important that the substrate possesses conductivity to be used as an electrode. As far as these requirements are concerned, a highly oriented pyrolytic graphite (HOPG) substrate surface is found to be suitable. Moreover, a HOPG surface is hydrophobic in nature. Hence, the nucleation and growth mechanism of polymers on a hydrophobic surface of HOPG can be investigated.

In recent papers, we discussed the nucleation and growth mechanism of polypyrrole on gold/HOPG and polyaniline on HOPG substrates at lower potentials using potentiostatic transient and AFM measurements [25, 27]. To our knowledge, studies on the nucleation and growth mechanism of polyaniline are limited to the potential range at which the formation of a layer of polyaniline is taking place, in order to be sure to examine the interaction between the electrode surface and polyaniline molecules. An analysis of data obtained at

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more anodic potential values allows the prediction of the mechanism for fast growing polyaniline. Hence, the aim of the present work is to find out the nucleation and growth mechanism for the electropolymerization of polyaniline at higher potentials on HOPG, based on the results obtained from potentiostatic transient and AFM measurements. Results obtained from the nucleation and growth mechanism of polyaniline at lower potentials are also presented for comparison.

Experimental

The electrochemical polymerization of aniline was carried out by a potentiostatic method, using a standard three-electrode cell. The HOPG working electrode used in this investigation has a surface area of 0.2375 cm^2 and was cleaved before use in all the experi-

ments. Platinum/titanium mesh and silver/silver chloride electrodes were used as counter and reference electrodes, respectively. The concentration of polyaniline was 0.02 M in all the experiments throughout the study; 0.04 M sulfuric acid was used as the supporting electrolyte solution. Before each experiment the supporting electrolyte was purged with nitrogen for about 30 min. Chronoamperometric measurements during anodic electrodeposition of polyaniline were controlled via a potentiostat (model 273A, EG&G, Princeton Applied Research) and recorded on a computer. The morphology of polyaniline deposited on HOPG was observed with a tapping mode atomic force microscope (Digital Instruments, Nanoscope III, $125 \mu\text{m}$ AFM scanning head). The material for the AFM cantilevers (Digital Instruments) was an edged single crystal of n-type silicon. The tip has a shape with 10 nm radius of curvature and 35° interior angle. Images were captured at a rate of 0.25 frame/min . During AFM measurements, considerable

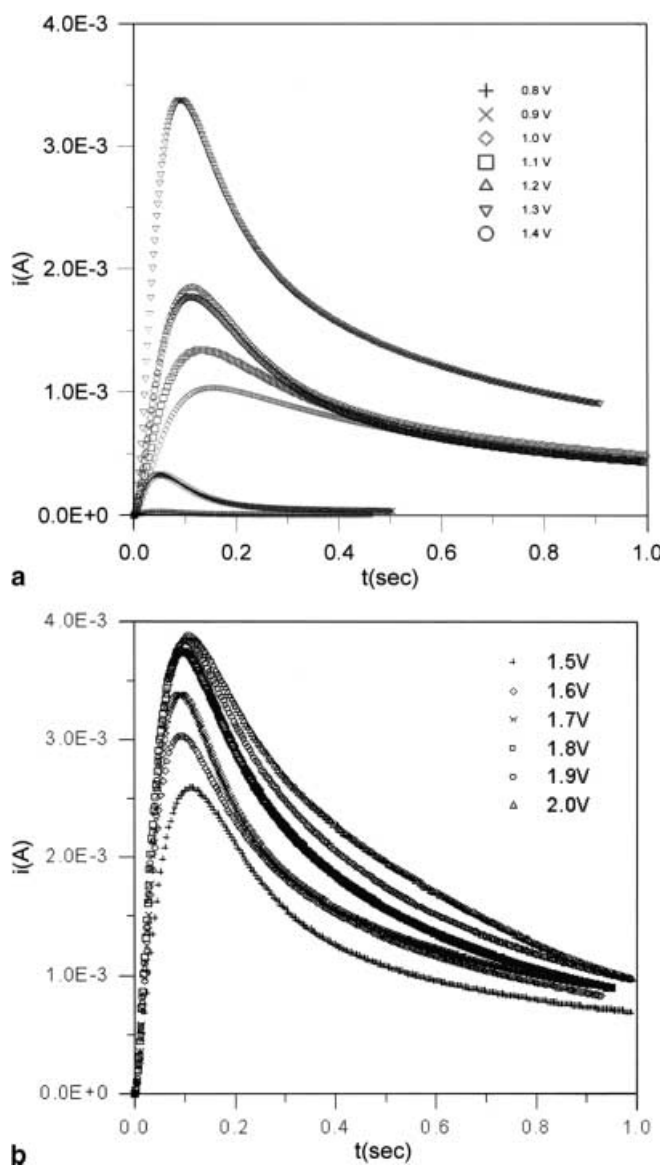


Fig. 1 Potentiostatic current-time transients obtained at a HOPG electrode in 0.02 M aniline/ 0.04 M H_2SO_4 solution: **a** at lower potentials and **b** at higher potentials

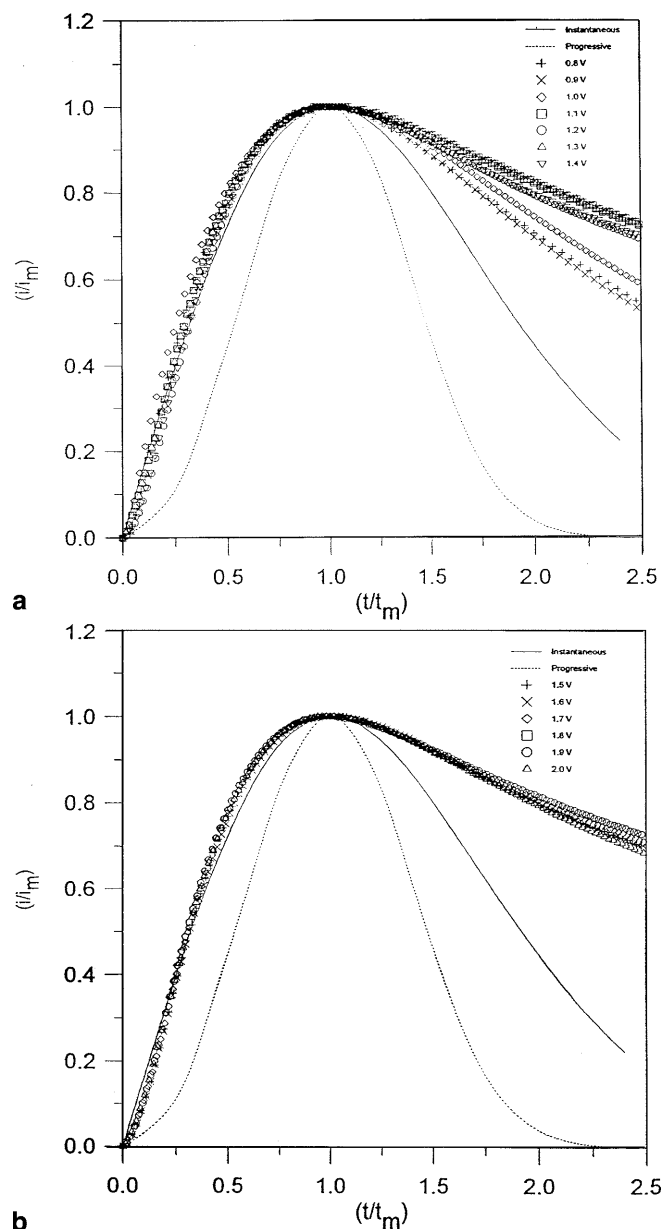


Fig. 2 Dimensionless plot of current maximum shown in Fig. 1 compared with theoretical curves for 2-D instantaneous and progressive nucleation: **a** at lower potentials and **b** at higher potentials

searching was done to find images on various parts of the surface and here we show the images that we could find in several parts on the surface. Most of the areas examined produced reproducible images similar to those shown in this paper.

Results and discussion

Figure 1a and b shows typical potentiostatic current-time transient curves obtained for polyaniline formation at different anodic potentials in the range 0.8–1.4 V and 1.5–2.0 V, respectively, vs. Ag/AgCl in 0.02 M aniline/0.04 M sulfuric acid solution at a HOPG substrate. At all the potentials studied, the transients show a pronounced current maximum. The value of the current maximum,

I_{\max} , increases with the increase of polymerization potential. This is due to the fact that the number of nuclei increases as the number of active sites for the polymerization of aniline increases when the potential is increased from lower to higher values. Moreover, the time of appearance, t_{\max} , decreases with the increase of the potential. This observation is attributed to the fact that the spread and collapse of the polyaniline nuclei occur more quickly at higher potentials.

The current maximum can be analyzed by comparing the experimental data with theoretical plots given for different types of nucleation processes. It is known that there are two types of nucleation, namely instantaneous and progressive, and two types of growth, 2-D and 3-D. Instantaneous nucleation is a process of nuclei formation at a high rate on a small number of active sites, whereas progressive nucleation is a different process of nuclei formation at a low rate but on a large number of active sites. Theoretical plots for progressive and instantaneous nucleation in 2-D and 3-D directions are given by the following equations [28]:

$$\begin{aligned} \text{2-D progressive: } I/I_{\max} &= (t/t_{\max})^2 \exp\{-0.67(t^3 - t_{\max}^3)/t_{\max}^3\} \end{aligned} \quad (1)$$

$$\begin{aligned} \text{2-D instantaneous: } I/I_{\max} &= (t/t_{\max}) \exp\{-0.5(t^2 - t_{\max}^2)/t_{\max}^2\} \end{aligned} \quad (2)$$

$$\begin{aligned} \text{3-D progressive: } (I/I_{\max})^2 &= 1.2254/(t/t_{\max}) \{1 - \exp[-2.3367(t/t_{\max})^2]\}^2 \end{aligned} \quad (3)$$

$$\begin{aligned} \text{3-D instantaneous: } (I/I_{\max})^2 &= 1.9542/(t/t_{\max}) \{1 - \exp[-1.2564(t/t_{\max})]\}^2 \end{aligned} \quad (4)$$

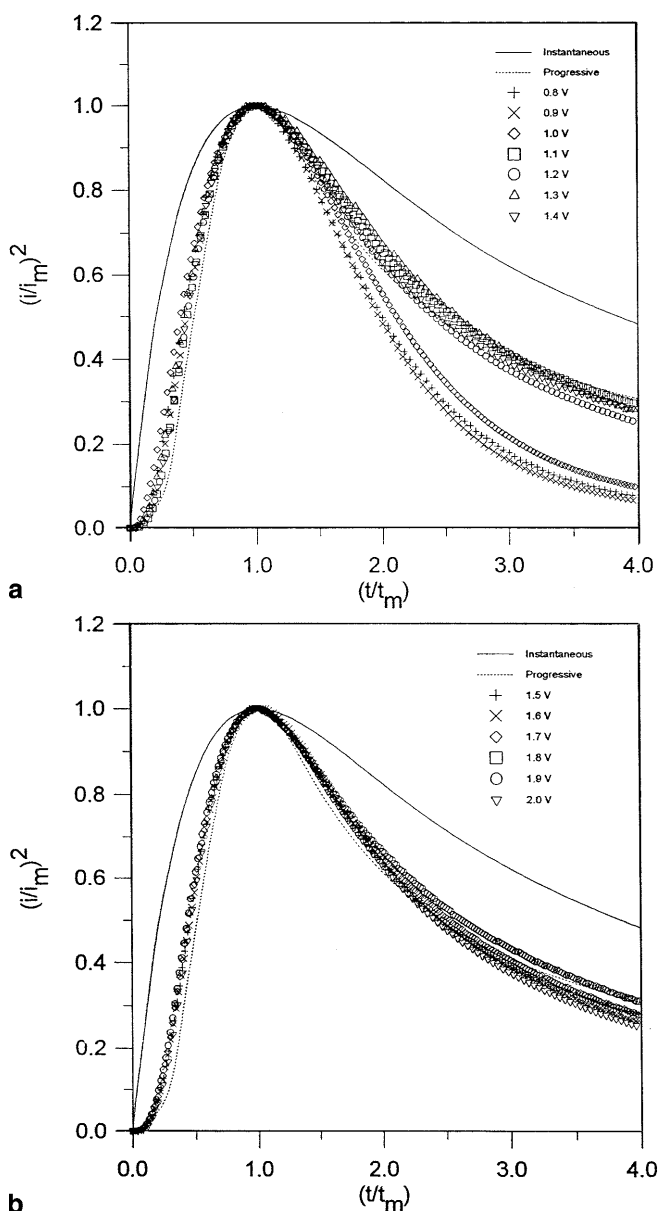


Fig. 3 Dimensionless plot of current maximum shown in Fig. 1 compared with theoretical curves for 3-D instantaneous and progressive nucleation: **a** at lower potentials and **b** at higher potentials

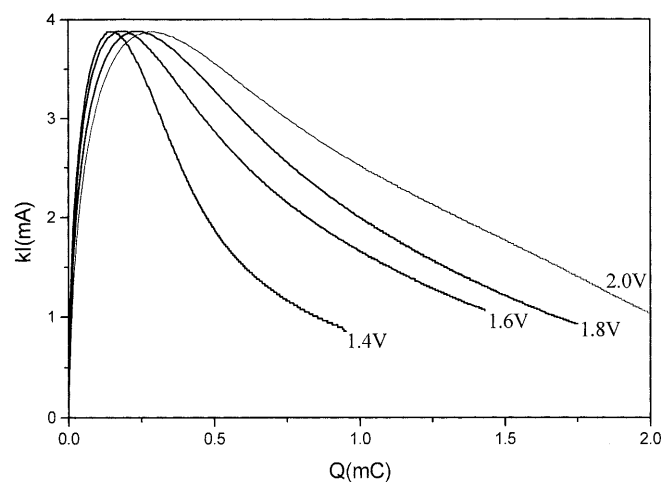
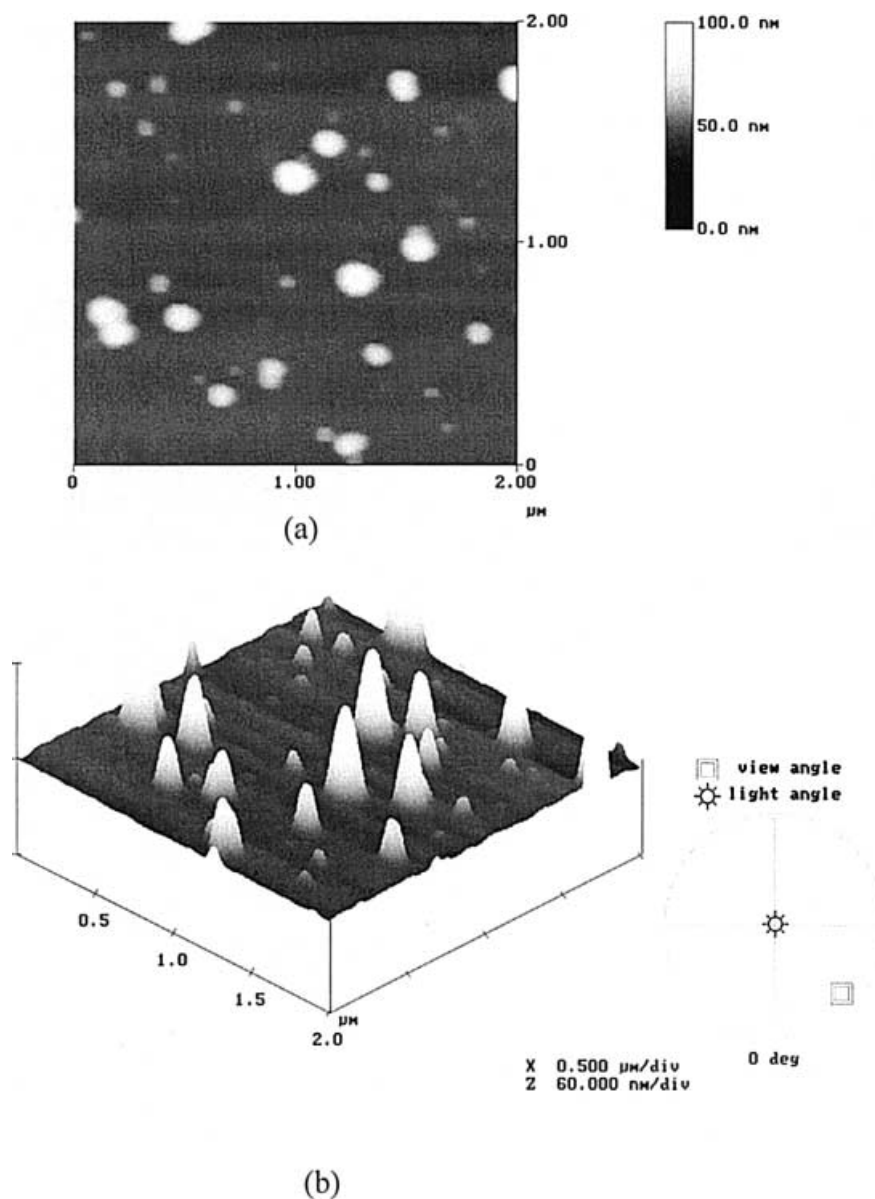


Fig. 4 The normalized current for the deposition of polyaniline at different positive potentials as function of charge passed (data from the measurements in Fig. 1). The current of each transient has been normalized by multiplying with a factor k such that $I_{\max}k = I_{\max,2.0 \text{ V}}$

Fig. 5 AFM images of polyaniline prepared with a deposition charge of 8.58 mC/cm^2 on HOPG at 1.5 V : **a** 2-D view and **b** 3-D view; scan scale: $2 \text{ }\mu\text{m}$

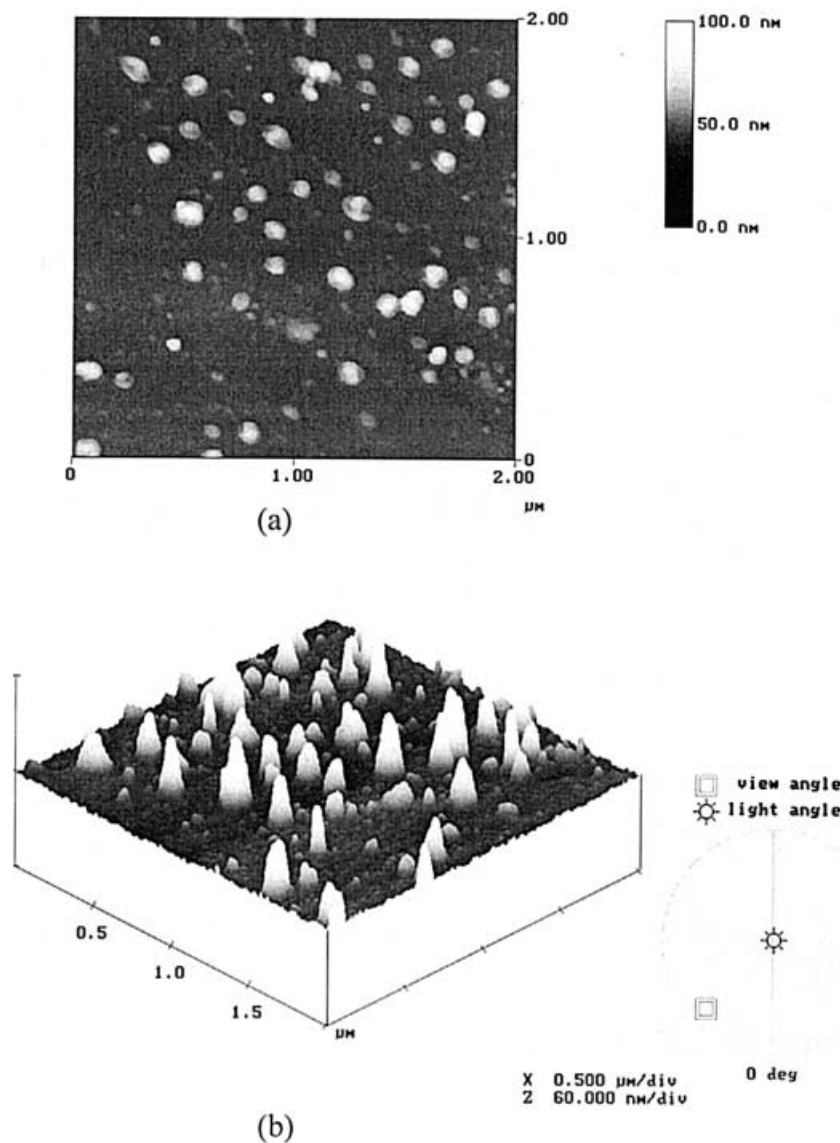


where the parameters t_{\max} and I_{\max} represent the coordinates of the current maximum.

The theoretical plots obtained from these equations are fitted to the experimental data obtained from current-time transient measurements for the electropolymerization of polyaniline at various lower as well as higher potentials. Figure 2a and b compares the dimensionless plots obtained from the experimental data with the theoretical plots for 2-D instantaneous and progressive nucleation at various lower and higher potentials, respectively. It seems that the experimental data more or less coincide with the theoretical plot of 2-D instantaneous nucleation before I_{\max} . However, after I_{\max} the experimental data abruptly deviate. Therefore, this attempt to use a 2-D instantaneous and progressive model for the interpretation of the experimental data failed to give satisfying results.

Then, it was tried to fit the experimental data with the theoretical plots of 3-D instantaneous and progressive nucleation processes. The fitted curves are shown in Fig. 3a and b at various lower and higher potentials, respectively. The experimental results obtained at higher potentials show good agreement with the theoretical plot of 3-D progressive nucleation. It is also seen that after I_{\max} the experimental plot for the electropolymerization of aniline deviates slightly above the theoretical curves of 3-D progressive nucleation when the potential is increased from 1.5 V to 2.0 V . This might be due to the increased conductance of the polyaniline phase, as the measurements were carried out at higher anodic potentials [9]. However, the experimental results obtained at lower potentials do not show good agreement with theoretical curves of 3-D progressive nucleation.

Fig. 6 AFM images of polyaniline prepared with a deposition charge of 10.73 mC/cm^2 on HOPG at 1.7 V : **a** 2-D view and **b** 3-D view; scan scale: $2 \mu\text{m}$



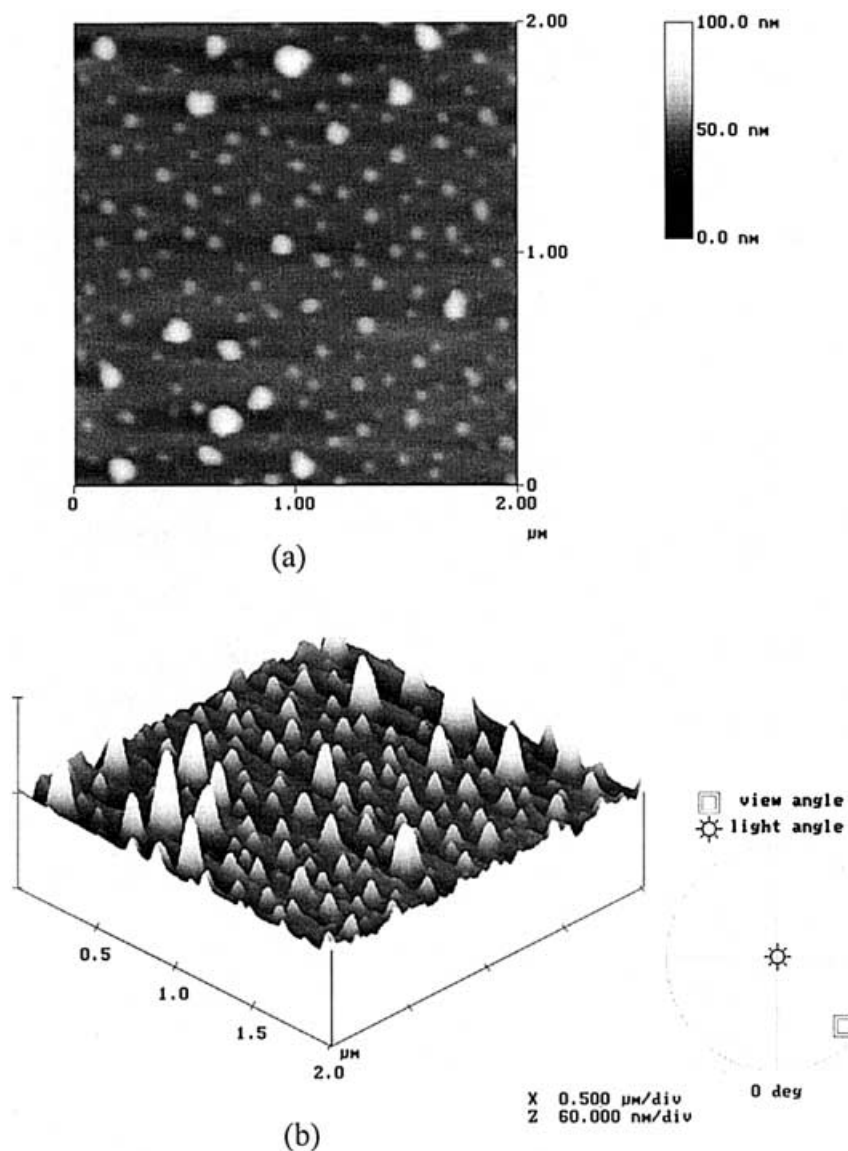
Then the results obtained at lower potentials were fitted to the theoretical curves for 2-D instantaneous and 3-D progressive nucleation. The nucleation and growth mechanism was found to be 2-D instantaneous, 3-D progressive and a combination of 2-D instantaneous and 3-D progressive at the rising part, at the current maximum and at the descending part of the curves, respectively. These results are described in detail elsewhere [27]. In this paper, the results obtained from higher potentials are discussed further.

Figure 4 shows a chronocoulometric analysis of the current-time transients obtained at different higher potentials. The effect of deposition potential can be analyzed from this figure. The decrease in the normalized current after the maximum at 1.4 V is faster. When the potential is increased from 1.4 V to 2.0 V , the conductivity of the film increases, as seen from the slower decrease in the normalized current after the current maximum. Hence, polyaniline films of different

conductivity can be produced with a proper control of the synthesis conditions. As seen in Fig. 4, the most conductive films are obtained at 2.0 V among the potentials studied.

Another experimental technique is essentially needed to verify the results obtained from potentiostatic current-time transient measurements. AFM has been found to be a suitable technique to analyze the kinetics and geometry of nucleation and growth. AFM measurements were carried out at all the potentials from 1.5 V to 2.0 V . Representative AFM images are shown in Figs. 5, 6, 7 at different potentials of 1.5 , 1.7 and 1.9 V , respectively, for the electropolymerization of aniline on HOPG. For comparison, all the images are shown in the same scanning size of $2 \mu\text{m}$. It is known that nuclei can grow in two alternative ways as in the case of metal deposition, namely 2-D and 3-D. From AFM images of the electropolymerization of aniline at different potentials (Figs. 5, 6, 7), it is clearly seen that the oligomer

Fig. 7 AFM images of polyaniline prepared with a deposition charge of 11.10 mC/cm^2 on HOPG at 1.9 V : **a** 2-D view and **b** 3-D view; scan scale: $2 \text{ }\mu\text{m}$



formed in the solution phase precipitates on the substrate surface as shiny deposits. Nuclei are thus formed and continue to grow and the growth rates of the nuclei are essentially comparable in the directions parallel and perpendicular to the electrode surface. It is also observed that the shape of the nuclei are conical. These are all the criteria for 3-D growth. Meanwhile, from the observation of AFM images, for example Fig. 7, it is clear that nuclei are formed on a large number of active sites. Nuclei of different sizes are also seen clearly. These observations conclude that the nucleation is progressive. Thus, the results obtained from potentiostatic current-time transient measurements, i.e. 3-D progressive nucleation, have also been verified from the results of AFM observations.

Now, it is indeed worthwhile to compare the results of the present work with our previous results and the results reported in the literature. To our knowledge, most of the work [22, 23] on nucleation and growth

mechanisms of polyaniline has been carried out at lower potentials. In all these studies, 2-D progressive nucleation [22], 3-D progressive nucleation and a combination of 2-D progressive and 3-D instantaneous in H_2SO_4 and HClO_4 have been reported, on gold or platinum electrodes. However, a HOPG substrate has a flat, conductive and hydrophobic surface to study the nucleation and growth mechanism. Hence, we have used a HOPG substrate in all our studies. According to Bade et al. [22], the nucleation and growth mechanism of polyaniline on a platinum electrode at a slightly higher potential of 1.0 V in H_2SO_4 media is 2-D progressive. Even though there is a possibility of overoxidation of polyaniline at higher potentials [29], we have made an attempt to observe the nucleation and growth mechanism of polyaniline in the potential range $1.5\text{--}2.0 \text{ V}$. As far as nucleation is concerned, our result for progressive nucleation is consistent with the result of Bade et al. but the growth is 3-D, in contrast to 2-D in their report.

When comparing literature results, differences in the nucleation and growth mechanism for electropolymerization of aniline may be due to a greater driving force for polymerization at more anodic potentials and hence vertical growth. Also, when comparing our results at lower potentials, i.e. a combination of instantaneous 2-D and progressive 3-D nucleation and growth, the progressive 3-D mechanism observed in this work is also believed to be due to the effect of higher anodic potentials, since a fresh HOPG substrate surface is used in each and every experiment throughout this work.

Conclusions

In the present work on the electropolymerization of aniline at higher potentials, the experimental data obtained from the potentiostatic current-time transient measurements were compared with the theoretical models for nucleation and growth. From this comparative evaluation it has been concluded that at higher potentials the growth of polyaniline is in the 3-D direction and the nucleation is progressive. These results have also been quite consistent with the images obtained from AFM measurements.

Acknowledgements The financial support from the National Science Council (NSC 88-CPC-E-011-008) and National Taiwan University of Science and Technology is gratefully acknowledged.

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