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Polypyrrole Growth on $YBa_2Cu_3O_{7-\delta}$ Modified with a Self-Assembled Monolayer of *N*-(3-Aminopropyl)pyrrole: Hardwiring the "Electroactive Hot Spots" on a Superconductor Electrode

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The cuprate high-temperature superconductors represent an important class of electronic materials which exhibit a variety of fundamentally interesting and technologically important properties. Many of the unusual features associated with these remarkable compounds can be traced to the anisotropic structures associated with these materials.[1] Important information related to the surface conductive properties of cuprate superconductor systems has been acquired from a variety of electrochemical studies.[2,3] Using such techniques, conductive polymer structures have been deposited onto cuprate superconductor electrodes.[3−7] Recent studies of conducting polymer/high-T_c superconductor structures have revealed a number of interesting electrical and electron transfer phenomena which occur at the polymer/superconductor interface.[3,5−7] However, it has become apparent from these prior studies that electrochemically polymerized polymers grow in a sporadic and sluggish manner when deposited onto *c*-axis films of the prototypical superconductor $YBa_2Cu_3O_{7-\delta}$.[4,6]

In this paper, we describe a new method for controlling the deposition of conductive polymer systems onto high-T_c superconductor surfaces. This method relies on the spontaneous adsorption of the pyrrole-terminated alkylamine reagent **1** onto $YBa_2Cu_3O_{7-\delta}$ prior to polymerization.[8] Large changes in the polymer growth rates and vast improvements in the polymer morphology are obtained with the use of such adsorbed monolayers. As will be described below, the adsorbed monolayer structures promote radically different polymer deposition properties from those observed previously for the more traditional electrode materials (i.e., Au, Pt, etc.). These unusual observations provided valuable insight into the electrochemical characteristics and local surface electroactivity/conductivity properties of oriented cuprate superconductor films.

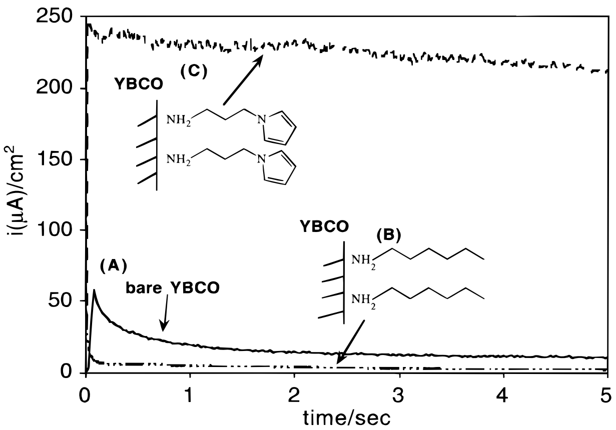

Figure 1. Chronoamperometry data for the polymerization of polypyrrole using a 0.1 M Bu_4NBF_4 in 1% (by volume) pyrrole/acetonitrile solution. The potential was stepped from a resting value of 0.0 to 1.0 V vs Ag wire (∼1.1 V vs SCE) for 5 s. Data is provided for *c*-axis $YBa_2Cu_3O_{7-\delta}$ films on MgO (100) substrates with a superconductor thickness in each case of ∼1500 Å. Experimental traces are provided for the following three cases: (A) untreated superconductor, (B) superconductor coated with a monolayer of hexylamine, and (C) superconductor coated with a *N*-(3-aminopropyl)pyrrole **(1)** monolayer.

For the polymer growth studies, *c*-axis-oriented $YBa_2Cu_3O_{7-\delta}$ thin films (∼1500 Å thick) were deposited onto single crystalline substrates of MgO (100) or $LaAlO_3$ (100) using the pulsed laser ablation technique.[9] The freshly deposited thin film electrodes were soaked in ∼1 mM acetonitrile solutions of *N*-(3-aminopropyl) pyrrole (**1**) or hexylamine (**2**) for 24 h and then thoroughly rinsed with acetonitrile to wash away excess physisorbed adsorbate reagent. Compound **1**, which is new and fully characterized,[10] was designed for the preparation of monolayer films on cuprate-based high-temperature superconductors.[8] Alkylamine reagents lacking the pyrrole moiety have been shown previously to form densely packed monolayer films on cuprate superconductors.[8a,b] Also, other studies have shown that a variety of functional groups can be anchored in a persistent manner through chemisorption processes onto high-T_c superconductor surfaces.[8c]

Polypyrrole was deposited onto $YBa_2Cu_3O_{7-\delta}$ thin films exploiting a potential step technique using a solution of 0.1 M Bu_4NBF_4 in 1% pyrrole/acetonitrile. A potential of 1.0 V vs Ag wire (∼1.1 V vs SCE) was applied to the $YBa_2Cu_3O_{7-\delta}$ electrode for 5 s to generate a thin polypyrrole layer.[11] The chronoamperometry data for three $YBa_2Cu_3O_{7-\delta}$ thin film electrodes—one bare, one modified with a monolayer of hexylamine, and one modified with a monolayer of **1**—are shown in Figure 1. Unlike the untreated superconductor surface where sluggish polymer growth is observed (Figure 1A), the surface modified with **1** promotes rapid polymer growth (Figure 1C). Here, nearly constant current behavior is noted following the initial charging of the double layer and nucleation events.[12] The continuous decrease in current noted for the unmodified and hexylamine-modified surfaces follows that expected for electrode structures where soluble monomer electrochemistry of monomeric species is dominant, whereby polymer coupling to the electrode occurs inefficiently, or where electrode passivation happens.[12]

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(11) Using the described electrochemical parameters, 300 Å for the average thickness was measured by profilometry for bare Au. Other sample thickness values of 10 Å for bare $YBa_2Cu_3O_{7-\delta}$ and 200 Å for *N*-(3-aminopropyl)pyrrole-coated $YBa_2Cu_3O_{7-\delta}$ were estimated from the measured current values recorded in the potential step experiments

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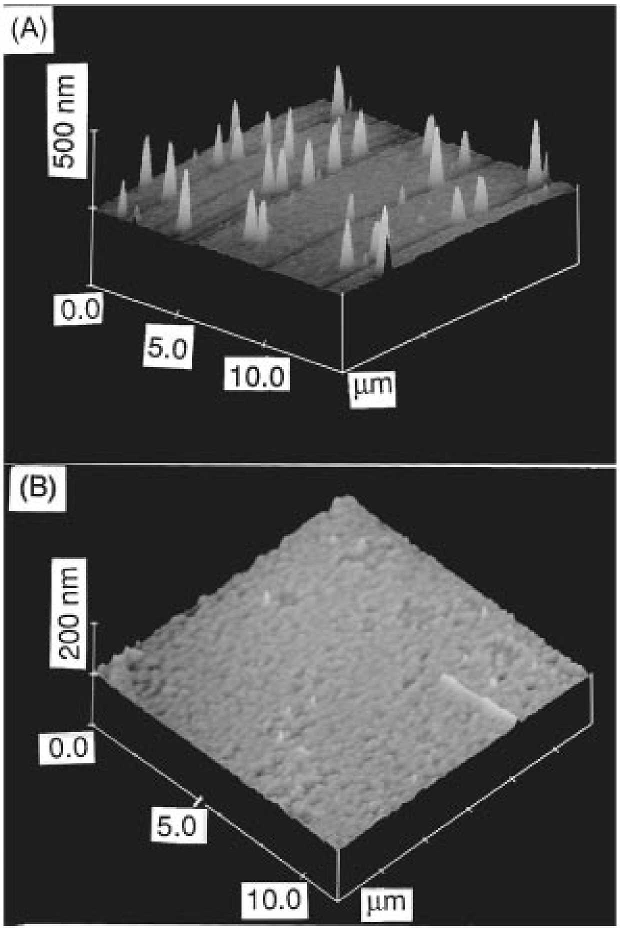

Figure 2. AFM images for *c*-axis-oriented films of $YBa_2Cu_3O_{7-\delta}$ on MgO (100) (1500 Å superconductor thickness) onto which polypyrrole layers were grown via the potential step procedure. Conditions were the same as those used to generate the data supplied in Figure 1. Images are provided for (A) untreated $YBa_2Cu_3O_{7-\delta}$, and (B) *N*-(3-aminopropyl)pyrrole-modified $YBa_2Cu_3O_{7-\delta}$.

To explore whether the increase in polymer growth rate was directly influenced by polymeric coupling to the surface-confined pyrrole moieties or simply a change in surface wetting and adhesion properties, the behavior of the hexylamine-modified surface **2** was evaluated under identical conditions (Figure 1B). Here, the measured current is much lower in magnitude than for the *N*-(3-aminopropyl)pyrrole-modified surfaces and the current continues to decrease with increasing time.[11] Clearly, the polymerization of pyrrole on bare and hexylamine-modified $YBa_2Cu_3O_{7-\delta}$ thin-film electrodes yields sluggish and nonuniform growth. The difference in the current−voltage transients for the *N*-(3-aminopropyl)pyrrole-modified surface as compared with the bare and hexylamine-modified surfaces suggests that the presence of the electroactive pyrrole monolayer greatly influences the polymer nucleation and growth rate. For longer polymerization times, the surface-localized polymer structures display reversible electrochemical doping/undoping characteristics on the cuprate films reminiscent of that observed previously for noble metal electrodes.[4] Interestingly, AFM and SEM images of polypyrrole layers grown under identical conditions onto films of *c*-axis $YBa_2Cu_3O_{7-\delta}$, with and without the pyrrole self-assembled monolayer, reveal that the *N*-(3-aminopropyl)pyrrole-modified surface produces thicker, more uniform, and more adherent layers. These differences are remarkable, as illustrated in the AFM images provided in Figure 2. The observation that ultrasmooth polymer layers are obtained with *N*-(3-aminopropyl)pyrrole-modified $YBa_2Cu_3O_{7-\delta}$ is consistent with the conclusion that polymer growth proceeds through rapid and uniform nucleation on the *N*-(3-aminopropyl)pyrrole-modified superconductor surface.[12]

Recent studies by the McCarley, Collard, Wrighton, and Rubinstein groups have shown that Au surfaces modified with pyrrole alkanethiol reagents exhibit large changes in polymer growth dynamics as compared with bare Au substrates.[13−16] Although significant differences in polymer morphology were observed for substrates modified with these pyrrole adsorbate molecules, little difference was noted in the chronoamperometry data for three Au electrodes (bare Au, Au coated with a linear alkylthiol, and Au modified with pyrrole alkanethiol[13]) which are analogous to the series of $YBa_2Cu_3O_{7-\delta}$ electrodes studied here. This observation, when compared with our data acquired at *c*-axis $YBa_2Cu_3O_{7-\delta}$ surfaces, provides important mechanistic information related to the room temperature electron transfer characteristics of *c*-axis $YBa_2Cu_3O_{7-\delta}$ electrodes (*vide infra*).

The presence of alternative crystallographic orientations of the $YBa_2Cu_3O_{7-\delta}$ lattice at localized defect sites in laser-ablated high-T_c films has been noted previously.[2] Accordingly, it is reasonable to conjecture that exposure of such "electroactive hot spots" to the electrolytic solution dominates the polymer growth dynamics at early polymerization time.

Upon modification of the high-T_c surface with (**1**) and subsequent electrochemically mediated oxidation, it appears that the surface sites, both electroactive hot spots (e.g., defect sites with exposed CuO_2 sheet edges), and relatively inactive areas (i.e., *c*-axis regions) become comparable in their ability to nucleate polymer growth. This behavior is likely due to the presence of the pyrrole monolayer serving to "hardwire" the electroactive hot spots on the $YBa_2Cu_3O_{7-\delta}$ surface, thereby forming a modified surface which displays more uniform electrochemical characteristics. The high surface concentration afforded by the adsorption of the pyrrole monolayer appears to promote this type of behavior. Alternatively, exposure of *a*-axis features caused during the adsorption of the amine reagent may be responsible for the observed behavior.

Moreover, evaluation of the early time periods ($t \leq 0.5$ s) of the current−time transients recorded for the polymer growth reveal an important electrode surface dependence of the early rate. Here, the following trend was noted for the polypyrrole nucleation/growth rates:

$$\begin{aligned}&N\text{-(3-aminopropyl)pyrrole-coated } c\text{-axis } YBa_2Cu_3O_{7-\delta} > \\ &\qquad \text{bare gold} > \text{bare } a\text{-axis } YBa_2Cu_3O_{7-\delta} > \\ &\qquad\qquad \text{bare } c\text{-axis } YBa_2Cu_3O_{7-\delta}\end{aligned}$$

Significantly, the *N*-(3-aminopropyl)pyrrole-modified surface displays more rapid polymer nucleation than that observed at the bare isotropic noble metal conductor Au. Furthermore, the poorly conductive *c*-axis surface of $YBa_2Cu_3O_{7-\delta}$ fosters more sluggish growth than the more conductive *a*-axis orientation.

These results demonstrate that judiciously chosen amine reagents can be used to enhance the immobilization of conducting polymer layers on cuprate superconductors. The monolayer system reported herein promotes good electrical, chemical, and physical contact between the polymer and superconductor component materials. These initial studies bode well for the preparation of superconductor/conducting polymer composite materials.

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Supporting Information Available: Synthesis, characterization, and schematic representation of polymer growth (3 pages). See any current masthead page for ordering and Internet access instructions.

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