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## Communications

### Molecular Level Control over the Surface and Interfacial Properties of High- $T_c$ Superconductors

John T. McDevitt,<sup>\*,†</sup> Chad A. Mirkin,<sup>\*,‡</sup>  
Rung-Kuang Lo,<sup>†</sup> Kaimin Chen,<sup>‡</sup> Ji-Ping Zhou,<sup>†</sup>  
Feng Xu,<sup>‡</sup> Steven G. Haupt,<sup>†,§</sup> Jianai Zhao,<sup>†</sup> and  
David C. Jurbergs<sup>†</sup>

*Department of Chemistry and Biochemistry  
The University of Texas at Austin  
Austin, Texas 78712, and Department of Chemistry  
Northwestern University, 2145 Sheridan Rd.  
Evanston, Illinois 60208*

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One of the major stumbling blocks that has plagued the practical utilization and fundamental studies of the high- $T_c$  cuprate superconductors has been the poor interfacial properties exhibited by these systems. Over 300 papers in the scientific literature document the reactivity problem of the cuprate superconductors with water, carbon dioxide, and carbon monoxide.<sup>1</sup> Development of reliable methods to control the interfacial properties of cuprate systems is particularly important now as the initial high- $T_c$  superconductor products approach the marketplace.<sup>2</sup> Herein, the spontaneous adsorption of alkylamines and fluorinated alkylamines onto the surface of cuprate-based compounds is reported. These monolayer films allow for control of the wetting properties, corrosion resistance, and adhesion characteristics of these superconductors. The molecules form densely packed, highly oriented structures on the

high- $T_c$  surfaces as evidenced by contact angle, X-ray photoelectron spectroscopy, X-ray reflectivity, and corrosion resistance measurements (vide infra). Thus, molecular level control over important surface and interfacial properties of cuprate superconductors is demonstrated.

The organization of molecular reagents into monolayer films on the surfaces of solid-state materials provides a convenient and rational approach toward controlling the surface and interfacial properties of these materials.<sup>3–20</sup> The best characterized and most extensively studied systems have involved linear alkanethiol reagents adsorbed onto gold and other noble-metal substrates.<sup>5,9,10,12</sup> The use of long-chain hydrocarbons

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<sup>†</sup> The University of Texas at Austin.

<sup>‡</sup> Northwestern University.

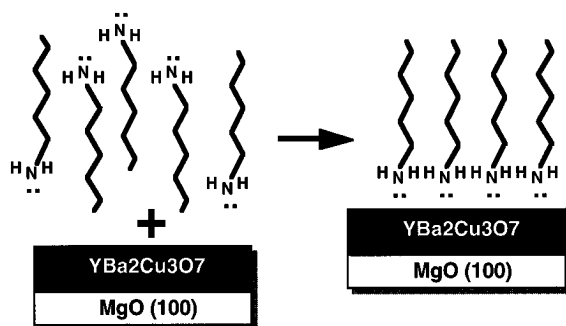
<sup>\*</sup> To whom correspondence should be addressed.

<sup>§</sup> Present address: Quantum Magnetism, 11578 Sorrento Valley Road, San Diego, CA 92121.

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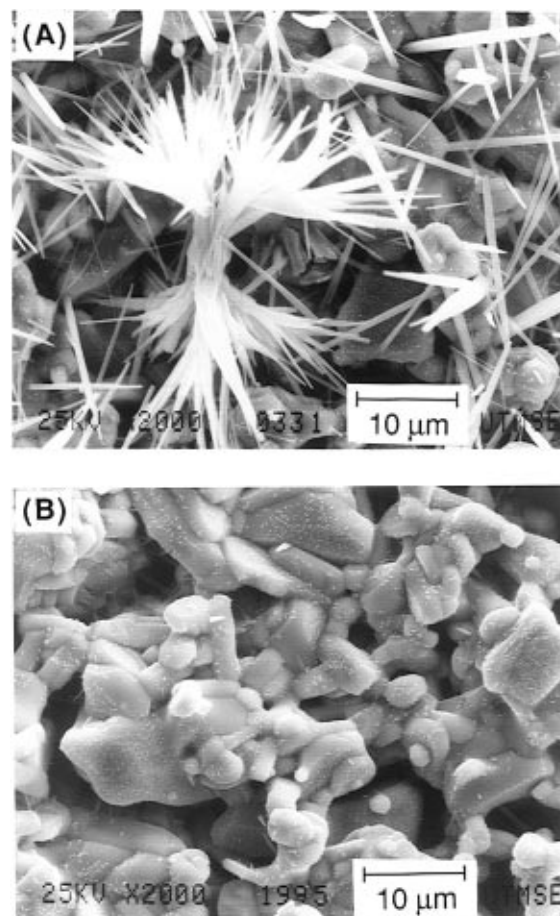
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Scheme 1



and crystalline substrates yields monolayers which are densely packed, oriented, and highly ordered. A recent survey of the surface coordination chemistry of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  has led to the identification of reliable methods for preparing persistent monolayers on the surface of a cuprate superconductor.<sup>21</sup>

Herein, we examine how carefully chosen adsorbate molecules, such as linear alkylamines and fluorinated alkylamines, can be used to tailor the corrosion resistance and surface adhesion properties of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (Scheme 1). To prepare the modified superconductor surfaces, freshly deposited  $\text{YBa}_2\text{Cu}_3\text{O}_7$  thin films<sup>22,23</sup> or freshly resurfaced ceramic electrodes<sup>24,25</sup> were exposed to solutions containing the amine reagents. This procedure leads to the formation of monolayer films with no measurable damage to the underlying superconductor substrate (i.e.,  $T_c$ ,  $\Delta T_c$ , and general surface morphology are unaffected as determined by four-point probe resistivity and AFM measurements, respectively). Accordingly, a great deal of experimental evidence is consistent with the hypothesis that densely packed, highly oriented monolayer structures are formed from the adsorption of linear alkylamines on  $\text{YBa}_2\text{Cu}_3\text{O}_7$ : (1) Contact-angle measurements with water and  $\text{C}_{16}\text{H}_{34}$  as wetting solvents on monolayers of linear alkylamines adsorbed on  $\text{YBa}_2\text{Cu}_3\text{O}_7$  yield values that are comparable to those obtained for monolayers of the analogous alkylthiol reagents adsorbed on gold.<sup>26</sup> (2) In previous studies, redox-active reagents adsorbed onto cuprate superconductors yielded electroactive layers with electrochemically assayed surface coverage values that were consistent with full monolayers after correcting for surface roughness.<sup>21</sup> (3) XPS measurements of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  samples that have been modified with  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{NH}_2$  show strong  $\text{F}(1s)$  signatures that are consistent with the modification of the surface with the fluorinated reagent. (4) Corrosive damage of the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  by  $\text{H}_2\text{O}$  is slowed in a dramatic fashion by the presence of linear alkyl- and fluorocarbon-amine monolayers (vide infra). (5) Adhesion of amorphous fluo-



**Figure 1.** Scanning electron micrographs of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ceramic pellets that were exposed to aerated water solution at room temperature for 1 day: (A) untreated pellet; (B) a similar pellet with a monolayer of  $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{NH}_2$  formed by soaking the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  sample in a  $\sim 1$  mM solution of  $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{NH}_2$  in acetonitrile for 24 h.

ropolymer (Teflon AF 1600, DuPont) layers to  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is increased significantly by first modifying its surface with a  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{NH}_2$  monolayer (vide infra).

Perhaps the most striking demonstration of the utility of the monolayer methodology for modification of the cuprate superconductor interfacial properties is shown in Figure 1. The illustration provides a dramatic comparison of the ability of a single monolayer formed from  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{NH}_2$  to exclude water from the surface of a high- $T_c$  ceramic pellet. Here, the uncoated  $\text{YBa}_2\text{Cu}_3\text{O}_7$  pellet degrades rapidly over a period of 1 day upon soaking in an aerated water solution, as evidenced by the formation of  $\text{BaCO}_3$ . This impurity phase collects on the surface of the superconductor, and its presence is visualized readily by scanning electron microscopy (i.e., the white crystals in Figure 1A). On the other hand,  $\text{YBa}_2\text{Cu}_3\text{O}_7$  modified with a monolayer of  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{NH}_2$  shows little sign of corrosion under identical conditions (Figure 1B). This result further supports the notion that the described procedures can be used to prepare densely packed adsorbate layers capable of excluding even small molecules such as water.

Although interesting from a fundamental point of view and as a short-term stabilization process, the use of a single monolayer for the long-term protection of superconductor structures is not a viable solution to the

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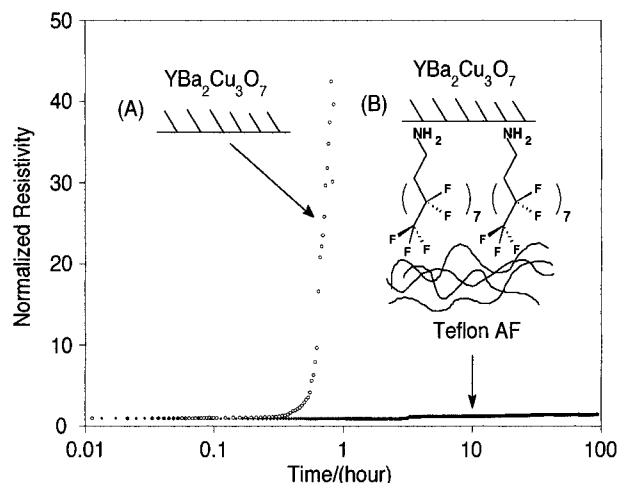
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**Figure 2.** Resistivity vs time measurements recorded for two  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (1500 Å) thin-film samples on MgO (100) substrates that were exposed to 75 °C water vapor and ~98% humidity. Data are provided both for an uncoated film and for a similar film that was coated with a monolayer of  $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{NH}_2$  onto which a 4  $\mu\text{m}$  thick Teflon AF polymer layer was coated.

corrosion problem. Rather, thicker polymer layers are expected to be more reliable for such an application. In this regard, amorphous fluoropolymer films would provide an ideal corrosion barrier. Unfortunately, the poor adhesion of fluoropolymers to oxide surfaces makes the use of such systems complicated.<sup>27</sup>

In an effort to improve the adhesion of amorphous fluoropolymers to cuprate surfaces, samples of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  were modified with monolayers of  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{NH}_2$ . Through this chemical modification of the superconductor surface, we have been able to prepare copper oxide superconductor surfaces to which an amorphous fluoropolymer layer adheres quite well as demonstrated by AFM.<sup>28</sup> Not surprisingly, the amorphous fluoropolymer layer is readily scratched away from the surface of the uncoated  $\text{YBa}_2\text{Cu}_3\text{O}_7$  sample. Although a small portion of the polymer is removed from the modified sample, the amount lost through the scanning process is a factor of ten less (as determined by AFM line scans across the pit region) than the experiment with unmodified  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

To explore the utility of the polymer and monolayer structures as corrosion barriers, the lifetimes of two  $\text{YBa}_2\text{Cu}_3\text{O}_7$  thin films were measured. Figure 2 shows the resistivity vs time measurements in a steam chamber for the two superconductor films with and without a  $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{NH}_2$  monolayer/Teflon AF polymer protection layer. Large increases in resistance of the uncoated sample are noted after about 1 h exposure time, indicating a rapid decomposition of the unprotected film under these accelerated corrosion conditions.

Similar measurements completed with only the monolayer coverage yield ~10-fold increase in the measured lifetime (not shown). On the other hand, the film modified with  $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{NH}_2$  monolayer/Teflon AF polymer displays marked improvement in stability with little increase in resistance over the entire 100 h period of the experiment. At this point, the sample was thermally shocked several times by treatment with liquid nitrogen and reintroduced into the chamber for another 50 h, again without noticeable degradation over the entire period of time. Samples coated with the same thickness of polymer layer but lacking the adhesive layer showed significant improvement relative to the bare and monolayer coated cases, but signs of contact failure (i.e., noisy data) were noted following ~48 h exposure time. Thus, the combination of polymer and adhesive monolayers provides a very effective barrier to slow the corrosion reactions of the cuprate thin films. Collectively, these results demonstrate that the monolayer-modified superconductor surface displays a strong propensity to adhere to the fluorinated polymer layer and the monolayer/polymer combination provides excellent corrosion protection.

In summary, a simple, yet powerful, method for controlling the interfacial properties of high- $T_c$  materials with densely packed monolayer films of fluorocarbon- and hydrocarbon-amine reagents has been demonstrated. Such monolayers have been shown to influence greatly the diffusion of molecular compounds such as  $\text{H}_2\text{O}$  to the superconductor surface. Thus, the corrosion resistance, adhesion, and wetting properties of the high- $T_c$  material can be tailored through judicious choice of adsorbate molecule. Polymer adhesion for packaging of superconductor products, corrosion protection layers, and device processing methods can be improved in a substantial manner with the chemistry reported herein.

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**Supporting Information Available:** AFM images and summary of contact-angle wetting data (4 pages). Ordering information is given on any current masthead page.

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