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Direct Oxidation of Alkylamines by $YBa_2Cu_3O_{7-\delta}$: A Key Step in the Formation of Self-Assembled Monolayers on Cuprate Superconductors

Jin Zhu and Chad A. Mirkin*

Department of Chemistry, Northwestern University
2145 Sheridan Rd., Evanston, Illinois 60201

Robert M. Braun and Nicholas Winograd*

Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

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Molecular monolayer-based surface modification chemistry, often referred to in the literature as "self-assembly", has been extensively developed and proven to be a remarkably useful methodology for the construction of well-defined organic surfaces and interfaces for three of the four important classes of electronic materials: metals, semiconductors, and insulators.[1] Recently, comparable but chemically distinct methodology has been developed for the fourth important class of electronic materials, cuprate-based high-temperature superconductors (HTSCs).[2] Since then, a great deal has been learned about the utility of these new surface structures for tailoring HTSC surface and interfacial properties. Monolayers of HTSCs have been used as hydrophobic layers for corrosion passivation,[3a] prelayers for improving polymer adhesion[3a] and crystal growth,[3b] polymer nucleation layers,[4] and as the barrier layers in tunnel junction devices.[5] The latter is a very important discovery because tunnel junctions form the heart of the developing HTSC industry and are the core device structures used to interrogate many of the intrinsic properties of HTSCs.

Among the functionalities surveyed thus far,[2a] alkylamines have been found to form the most robust monolayer structures, and all of the above-mentioned applications have been based on monolayers formed from molecular reagents with this functional group. Therefore, a detailed understanding of the reaction between $YBa_2Cu_3O_{7-\delta}$ and alkylamines is especially important in order to obtain a better understanding of this important monolayer self-assembly process. Described herein are the results of experiments aimed at elucidating this coordination chemistry. On the basis of previous electrochemical experiments[2a] and Raman spectroscopy,[6] it is known that amines chemisorb onto $YBa_2Cu_3O_{7-\delta}$ to form strong surface adsorbate interactions. To date, however, little is known about this reaction, including the chemical fate of the amine and superconductor as well as the preferred adsorbate binding site. In general, the surface coordination chemistry of inorganic materials is a very difficult problem to solve; indeed, with over 15 years of effort devoted to determining the interaction between alkanethiols and Au, there is still debate over the nature of this reaction.[7] Herein, we show that an extraordinary, but very clean redox reaction takes place between alkylamines and the highly oxidized surface of $YBa_2Cu_3O_{7-\delta}$ prior to chemisorption of the monolayer. Moreover, we report secondary ion mass spectrometry (SIMS) data, which provide evidence for the final chemical state of the adsorbate and its preferred surface binding site. Taken together, these preliminary studies provide the basis for understanding this complex but useful reaction.

In a typical experiment, $YBa_2Cu_3O_{7-\delta}$ powder (Strem Chemical Co.; average size 0.2 μm) was stirred in a solution of a primary alkylamine (0.16 M $CH_3(CH_2)_5NH_2$ in CH_3CN) for 2 days under N_2 atmosphere. The powder was then filtered, and CH_3CN was removed under vacuum. GC-MS was used to characterize the organic product from the reaction. The retention time of $CH_3(CH_2)_5NH_2$ on the 5% phenylmethylsiloxane column was 3.92 min, and the mass spectrum of $CH_3(CH_2)_5NH_2$ exhibits the expected M^+ ion at *m/z* 101, Figure 1A. After the reaction, a new peak in the GC analysis of the solution emerged at 8.10 min in addition to the peak at 3.92 min for unreacted $CH_3(CH_2)_5NH_2$. This product is assigned as the dialkylimine, $CH_3(CH_2)_4CH{=}N(CH_2)_5CH_3$, based on (1) the $[M - H]^+$ ion as observed at *m/z* 182 and (2) a comparison of its mass spectrum with that for an authentic sample of the dialkylimine, which was independently synthesized in our laboratories.[8] These spectra are shown in parts B and C of Figure 1, respectively. In addition, GC analysis of $CH_3(CH_2)_4CH{=}N(CH_2)_5CH_3$ shows that it exhibits a retention time identical to that for the product generated from the reaction between $YBa_2Cu_3O_{7-\delta}$ and *n*-hexylamine.

X-ray photoelectron spectroscopy (XPS) was used to characterize the $YBa_2Cu_3O_{7-\delta}$ powder before and after the surface modification reaction (takeoff angle = 45°). Powder samples of $YBa_2Cu_3O_{7-\delta}$, unmodified and modified with *n*-hexylamine, were pressed into pellets in order to facilitate XPS studies. The XPS spectra of the powder before and after modification with *n*-hexylamine clearly show that a redox reaction is occurring between the amine and superconductor. The ratio of the O 1s peak to Ba $3d_{3/2}$ peak decreases from 1.15 to 0.78 upon surface modification. This ratio is a signature of surface reduction and loss of oxygen. Although there are no unambiguous XPS signatures which differentiate Cu(III) and Cu(II),[9] either Cu(III) or peroxide, the two cited potential oxidizing sites in the superconductor,[9] must be reduced in this process to form Cu(II) or oxide, respectively. Both of these processes would result in concomitant loss of oxygen from the superconductor. If Cu(III) is involved, the reaction stops at Cu(II) as evidenced by the signature $2p_{3/2}$ and $2p_{1/2}$ shake-up features in the XPS spectrum of the modified material (i.e., there is no evidence for formation of Cu(I) or Cu(0)).[10] Consistent with this hypothesis, cyclohexylamine reacts with Cu(II) to form a stable coordination complex, $[Cu(C_6H_{11}NH_2)_4]^{2+}$ (i.e., Cu(II) does not oxidize the alkylamine).[11]

The bulk structure of $YBa_2Cu_3O_{7-\delta}$, before and after treatment with *n*-hexylamine, was characterized by powder X-ray diffraction (XRD). There is no significant change in the phase structure of the $YBa_2Cu_3O_{7-\delta}$ as evidenced by virtually identical XRD patterns for the modified and unmodified samples, at least under the conditions used herein. Moreover, there is no change in the critical temperature (92 K), as determined by SQUID, for these materials even after they have been modified under these conditions (see Supporting Information). This indicates that in

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* Address correspondence to: camirkin@chem.nwu.edu.

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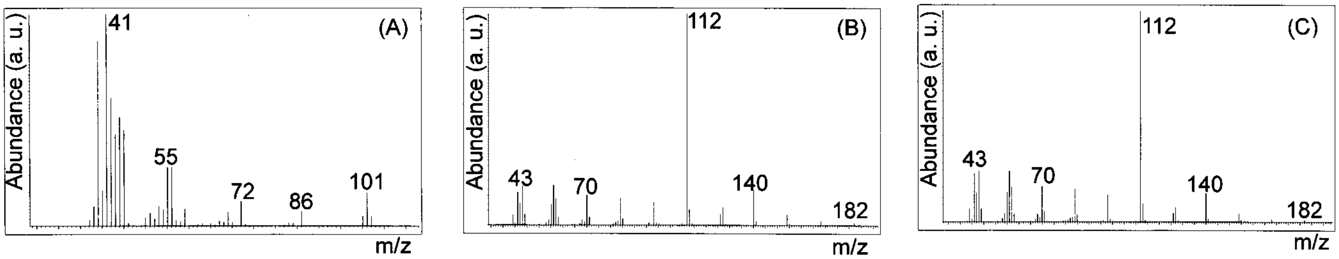


Figure 1. GC-MS of (A) the starting compound $CH_3(CH_2)_5NH_2$, (B) the only detectable organic product from the reaction between $YBa_2Cu_3O_{7-\delta}$ powder $CH_3(CH_2)_5NH_2$ in acetonitrile, and (C) an independently synthesized sample of $CH_3(CH_2)_4CH{=}N(CH_2)_5CH_3$.

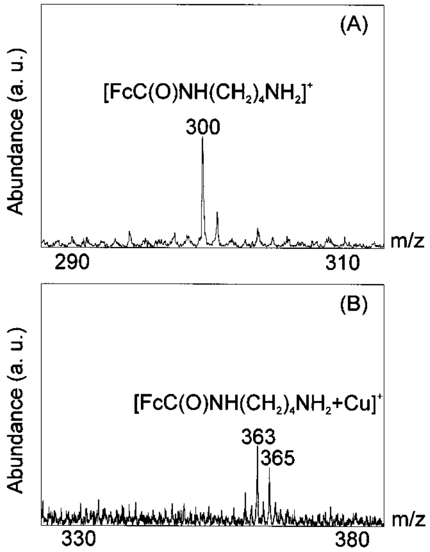
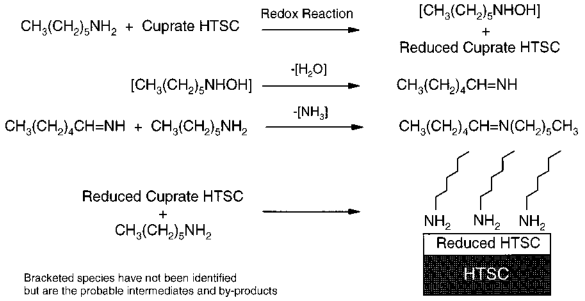


Figure 2. Two regions of the positive-ion secondary ion mass spectrum of a $YBa_2Cu_3O_{7-\delta}$ surface after modification with $FcC(O)NH(CH_2)_4NH_2$: (A) the region between *m/z* 288 and 312 showing the molecular ion (M^+) for the amine and (B) the region between *m/z* 328 and 382 showing the $[M + Cu]^+$ peak at 363 *m/z* with the expected isotopic pattern for Cu.

the monolayer "self-assembly" process the redox reaction primarily affects the chemical state of the superconductor surface, without causing significant reduction of the bulk material.

To further characterize the nature of the adsorption process, SIMS was used to study the superconductor surface after chemical modification. SIMS has been used extensively to characterize chemically modified surfaces and can provide information regarding the chemical fate of the adsorbate and, in some cases, the preferred surface binding site(s).[12] In these studies, we used an alkylamine with a Fc reporter group, $FcC(O)NH(CH_2)_4NH_2$ (Fc = Ferrocenyl), which allows us to confirm adsorption independently by electrochemical methods.[2] The positive-ion mode SIMS spectrum of a ceramic $YBa_2Cu_3O_{7-\delta}$ surface modified with $FcC(O)NH(CH_2)_4NH_2$ exhibits two very informative peaks in addition to a variety of background peaks associated with the inorganic substrate (not shown), Figure 2, parts A and B. An M^+ peak was observed at *m/z* 300 showing that the amine, and not imine oxidation product, adsorbs onto the reduced superconductor surface, Figure 2A. In addition, a $[M + Cu]^+$ peak is observed at *m/z* 363 with the expected Cu isotope distribution. No peaks were observed for $[M + Ba]^+$ and $[M + Y]^+$ fragments, which when combined with previous indirect evidence,[2b] strongly suggests that the preferred sites of amine binding for this superconducting oxide are Cu^{2+} atoms. Although it is possible for close, neighboring fragments to combine in the SIMS experiment,[13] the only atoms in this plane of the superconductor other than Cu are O atoms, and it is unlikely that the amine bonds to them.

Scheme 1



Taken together, our data support the following mechanism for the self-assembly of monolayers of alkylamines on $YBa_2Cu_3O_{7-\delta}$. The surface is initially reduced (Cu^{3+} to Cu^{2+} or peroxide to oxide) by the alkylamine, which results in formation of the dialkylimine, $CH_3(CH_2)_4CH{=}N(CH_2)_5CH_3$, and concomitant loss of oxygen from the superconductor. The oxidation of an alkylamine to alkylimine by inorganic oxidants in the presence of O_2 is a well-known process and often occurs through initial formation of a hydroxyamine, which is unstable and loses H_2O to form an imine. In the case of the $YBa_2Cu_3O_{7-\delta}$ oxidation of *n*-hexylamine, the initial product is $CH_3(CH_2)_4CH{=}NH$. Note that in some cases this product could be detected by GC-MS, but is clearly an intermediate that is consumed as it forms. This imine reacts with another equivalent of *n*-hexylamine to form the observed dialkylimine, $CH_3(CH_2)_4CH{=}N(CH_2)_5CH_3$, and presumably NH_3.[14] After initial reduction of the surface, another equivalent of alkylamine binds to the surface at Cu^{2+} sites to form a monolayer film. Although the precise thickness of the reduced surface layer is not known, it must be very thin (<20 Å) because these monolayers form adequate tunnel junction barrier layers.[5] In fact, these experiments suggest that in the fabrication of SIN (superconductor/insulator/normal metal) tunnel junctions from self-assembled monolayers of alkylamines, the junction layer is a combination of a thin reduced superconductor layer and the organic film.

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Supporting Information Available: Figures showing the XPS of $YBa_2Cu_3O_{7-\delta}$ and the Cu 2p region and SQUID magnetization measurements for $YBa_2Cu_3O_{7-\delta}$ (3 pages, print/PDF). See any current masthead page for ordering information and web access instructions.

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