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Structure and self-assembly of sequentially adsorbed coronene/octanethiol monolayers

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ABSTRACT

Scanning tunneling microscopy is used to investigate the structure of sequentially adsorbed coronene/octanethiol monolayers on Au(111). In these experiments, coronene-covered gold surfaces are exposed to octanethiol vapor. The resulting mixed monolayers are covered by close-packed octanethiol domains with clusters of coronene located within octanethiol domain boundaries. For these systems, the positions of coronene on the surface are determined by the kinetics of octanethiol monolayer formation and the local structure of the gold. The initial coverage and order of the coronene-covered surface influence the final structure of the mixed coronene/alkanethiol monolayer: deposition of coronene from the vapor phase, which creates a relatively lower coverage and higher degree of order than solution-based deposition, results in smaller coronene clusters. Statistical analysis of the locations of clusters of coronene shows that depending on the deposition parameters, coronene clusters are repelled in varying degree by upward-going and downward-going steps or are attracted to the top edges of surface step defects. In contrast to clusters, isolated coronene molecules are observed in the middle of close-packed octanethiol domains, but also appear to have an affinity for the edge of downward-going steps. We compare these results to mixed monolayers composed of C_{70} and octanethiol.

1. Introduction

Self-assembly of molecules into ordered two- and three-dimensional structures is of increasing interest for potential applications in materials science and nanotechnology [1–9]. In general, non-bonding intermolecular interactions such as van der Waals forces [10,11], hydrogen bonding [12,13], and π-stacking [14–16] drive self-assembly. Most studies of self-assembly have relied on strong intermolecular interactions that lead to ordering when the system settles into its lowest free-energy state.

Nuzzo and Allara introduced the formation of ordered alkanethiol (as well as other organosulfur) monolayers on gold as prototypical self-assembling systems. In the alkanethiol-gold system, strong sulfur–gold bonds anchor molecules to the surface and van der Waals interactions produce an ordered monolayer [17–20]. Alkanethiol monolayers have a rich phase structure [21–31]. A variety of striped phases, where molecules lie parallel to the gold surface, are observed at low coverage. As the coverage increases, octanethiol molecules stand up in order to maximize chain–chain interactions and surface sulfur density, resulting in a number of close-packed phases, characterized (to zeroth order only) by $(\sqrt{3} \times \sqrt{3})$ R30° symmetry. In addition to thermodynamic factors, the kinetics of monolayer formation play a partial role in the overall surface structure [20,25,26,32–34]. Alkanethiol monolayers on gold are highly polycrystalline, with the extent of long-range order determined by the preparation method and by post-fabrication processing (e.g. annealing) [35–40].

In this manuscript, we report on a study designed to emphasize the kinetic factors in monolayer formation, aimed at investigating whether kinetic constraints could provide a new approach for tailored surface modification. In our experiments, coronene ($C_{24}H_{12}$C) and octanethiol are sequentially deposited onto the Au(111) surface: a monolayer of coronene is formed first, followed by exposure to octanethiol. Octanethiol interacts with the surface more strongly than coronene, and it is thermodynamically preferred for octanethiol molecules to displace coronene from the surface. However, the presence of an already-formed coronene monolayer creates a significant energy barrier to displacement and alkanethiol monolayer formation.

Previous studies of self-assembly in multicomponent systems have shown that complex surface patterning can be achieved [41–48]. Recently, Wu and Zhang studied the replacement of coronene on Au (111) by 6-mercapto-1-hexanol (MHO) in solution [49]. The solution facilitates the removal of the coronene on the surface, allowing for replacement by MHO. The concentration of the MHO dictated the speed of the replacement.

Kinetic constraints can potentially provide new methods for investigating and controlling monolayer formation and properties. This degree of control is generally missing in systems where molecules and surfaces are carefully chosen to produce a desired and thermodynamically favored structure, as for any given molecule/surface system, there is only one structure that minimizes free energy globally. In contrast,

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there are potentially a large number of structures that minimize the free energy locally, each with its unique set of properties. We address these kinetic limitations to better understand the monolayer formation process and potentially to exploit the process to create kinetically trapped structures with desired properties.

This study extends previous measurements in our laboratory of sequentially deposited monolayers of C_{70} and octanethiol [50]. In those experiments, we deposited C_{70} onto Au(111), followed by octanethiol vapor deposition. Scanning tunneling microscopy (STM) images of the resulting mixed monolayers revealed close-packed domains and vacancy islands typical of octanethiol films, as well as a substantial decrease in C_{70} coverage. The remaining C_{70} formed small molecular clusters preferentially located at the top of surface step defects; clusters were also found within octanethiol domain boundaries. However, C_{70} were absent from the bottoms of step edges. The asymmetric distribution of fullerene molecules near step defects was attributed to the kinetics of octanethiol monolayer formation, where octanethiol nucleation at the bottom of step defects forced these areas to be clear of fullerenes.

Polycyclic aromatic hydrocarbons are, like fullerenes, graphene-based molecules with extended conjugated π-electron systems, and adsorption geometries on metals place planar molecules parallel to the surface at low coverages [51–59]. When adsorbed parallel to the surface, then, the strong π-electron interaction would argue for similar bonding when comparing C_{70} to coronene, the molecule chosen for the current study. We estimate a binding energy for coronene on Au(111) based on TPD measurements of related molecules, scaled by the number of sp^2 carbons; this approach is validated by direct calorimetric measurements of benzene and naphthalene on Pt(111), which show linear scaling [60,61]. On Au(111), adsorption energies for benzene [62,63], pentacene [57], and naphtho[2,3-a]pyrene [64] on Au(111) are 0.60, 1.14, and 1.06 eV, respectively. This corresponds to a per-sp^2-carbon binding energy on gold between 44.2 meV (naphthopyrene) and 100 meV (benzene), and from this we extrapolate 1.06–2.40 eV as an estimate for the binding energy of coronene on Au(111). We suggest that the higher end of this range is more relevant for the current study, as the measurements for pentacene and naphthopyrene were made at monolayer coverages where higher densities may result in weaker molecule-surface interactions. In comparison, C_{60} has a binding energy of 1.4–1.8 eV on Au(111), and packs at a surface density 33% greater than that of coronene [65–68]. Both fullerenes and coronene, then, show strong non-bonding adsorption of comparable magnitude. Alkanethiols adsorb significantly more strongly on Au(111) than either, with a Au–S bond strength of 1.30 eV [27], and a packing density 4 times that of C_{60} and 5.3 times that of coronene.

Once adsorbed, intermolecular interactions between coronenes or between fullerenes are likely to be significantly different. C_{70} retains strong van der Waals and charge-transfer interactions, while the C–H··H–C interactions between adsorbed coronenes will be quite weak. Comparing the structure of C_{70}/octanethiol and coronene/octanethiol mixed monolayers will help probe the effects of the weaker intermolecular interactions in the coronene/octanethiol system.

2. Experimental

The samples in this manuscript were prepared similarly to those made by Deering and Kandel [50]. For these studies, coronene is either drop-cast or vapor deposited onto a clean Au(111) substrate. This results in partial monolayers, monolayers, or multilayers of coronene, depending on the deposition method; this will be discussed in detail in the Results section. After deposition of coronene, the sample is exposed to octanethiol vapor.

Au(111)-on-mica substrates (Agilent Technologies) were annealed in a hydrogen flame and allowed to cool down prior to use. For drop-cast samples, coronene (Aldrich, 97%) was dissolved in toluene at <1 mM concentrations. A few drops of this solution were placed on a freshly annealed gold substrate. As the solvent evaporates, coronene remains on the gold surface. For vapor-deposited samples, a Au(111)-on-mica substrate and solid coronene are placed in a sealed vial and heated for 24 h at 125 °C.

Coronene/Au(111) samples, regardless of preparation method, were then exposed to octanethiol vapor (Aldrich, 98.5%) for 18–24 h at 70 °C. Octanethiol vapor deposition ensures that neither solvent or liquid octanethiol will contact the coronene. As a result, desorption of coronene from the surface must occur in the gas phase, which is prevented by the significant activation energy for this process. Disordered and partial monolayers of coronene are desorbed from the surface at 150 °C, which is significantly higher than the 70 °C used for octanethiol vapor deposition [69,70].

Images were acquired with a home-built scanning tunneling microscope controlled by commercial electronics (RHK Technology). All imaging is carried out at ambient temperature and pressure. The STM is operated at constant current using a tunneling bias of 0.5 V and a tunneling current of 10–20 pA. STM tips were made from mechanically cut Pt/Ir wire. Initial processing of the STM images consisted of removing noise along the fast-scan direction using a masked high-pass fitting procedure [71].

Images of both the drop-cast and vapor-deposited coronene monolayers on Au(111) were obtained in an ultra-high-vacuum (UHV) STM (base pressure of 10^{-9} Torr) at constant current with a tunneling bias of 0.5 V and a tunneling current of 5 pA.

3. Results

As described in Section 2, each experiment begins with a coronene-covered gold surface. Vapor-deposited coronene has been shown to lie in a flat orientation on Au(111) and form a commensurate 4×4 hexagonal superstructure [72]. Other coronene STM studies are done *in situ* and involve the immersion of Au(111) into a coronene-containing solution of benzene [73,74]. Uemura et al. made Langmuir films from dissolved coronene in benzene [75]. Hipps and coworkers, studying various alkanoic acids and coronene on Au(111), were able to form a high-density coronene structure [76,77]. All of these studies observed the formation of a well-ordered coronene monolayer.

In our approach, we deposit coronene through solution drop-casting and vapor deposition. Fig. 1 shows typical images of the coronene/Au(111) surface obtained via both methods, respectively. Samples are placed into a UHV STM for imaging only until after coronene deposition has occurred and samples have been allowed to cool down if needed. In both panels, we find ordered circular features about ~10 Å in diameter. On the basis of their size and uniform appearance, we assign them as molecular coronene features.

The image of the vapor-deposited coronene in Fig. 1b shows long-range order and uniformity of the molecular features. Rippling of the reconstructed gold surface can also be seen, as can several brighter spots attributable to impurities or defects. We cannot definitively rule out multilayer formation, but multilayers can desorb at temperatures above 100 °C, and our samples were formed at 125 °C [69,70]. The measured distance between coronene molecules in the vapor-deposited samples is 12.35 ± 1.04 Å, within error of the previously reported 4×4 structure. We believe that our image is consistent with formation of reasonably well-ordered coronene monolayers, as observed by other research groups [73–77].

We have found that drop-cast monolayers are generally substantially less ordered than those made through vapor deposition; this can be seen in Fig. 1a, where order is short range and many molecular features appear elongated. In ordered regions, the measured distance between coronene molecules is 13.17 ± 0.84 Å, however, these regions rarely extend to more than 10 molecules. This again fits with a 4×4 structure, at least within these small ordered areas; a more detailed analysis of the surface packing will be presented in the Discussion section. This matches our previous experience with fullerene monolayers, where drop-cast surfaces do not