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Self-Assembly of Alkanols on Au(111) Surfaces

Hai-Ming Zhang, Jia-Wei Yan, Zhao-Xiong Xie,* Bing-Wei Mao, and Xin Xu*[a]

Abstract: Self-assembled monolayers (SAMs) of alkanols (1-$C_NH_{2N+1}OH$) with varying carbon-chain lengths (N = 10–30) have been systematically studied by means of scanning tunneling microscopy (STM) at the interfaces between alkanol solutions (or liquids) and Au(111) surfaces. The carbon skeletons were found to lie flat on the surfaces. This orientation is consistent with SAMs of alkanols on highly oriented pyrolytic graphite (HOPG) and MoS_2 surfaces, and also with alkanes on reconstructed Au(111) surfaces. This result differs from a prior report, which claimed that 1-decanol molecules (N = 10) stood on their ends with the OH polar groups facing the gold substrate. Compared to alkanes, the replacement of one terminal CH_3 group with an OH group introduces new bonding features for alkanols owing to the feasibility of forming hydrogen bonds. While SAMs of long-chain alkanols ($N > 18$) resemble those of alkanes, in which the aliphatic chains make a greater contribution, hydrogen bonding plays a more important role in the formation of SAMs of short-chain alkanols. Thus, in addition to the titled lamellar structure, a herringbone-like structure, seldom seen in SAMs of alkanes, is dominant in alkanol SAMs for values of $N < 18$. The odd–even effect present in alkane SAMs is also present in alkanol SAMs. Thus, the odd N alkanols (alkanols with an odd number of carbon atoms) adopt perpendicular lamellar structures owing to the favorable interactions of the CH_3 terminal groups, similar to the result observed for odd alkanes. In contrast to alkanes on Au(111) surfaces, for which no SAMs on an unreconstructed gold substrate were observed, alkanols are capable of forming SAMs on either the reconstructed or the unreconstructed gold surfaces. Structural models for the packing of alkanol molecules on Au(111) surfaces have been proposed, which successfully explain these experimental observations.

Keywords: gold · physisorption · scanning probe microscopy · self-assembly · surface science

Introduction

Self-assembled monolayers (SAMs) of functional molecules on solid surfaces have been intensively investigated by using scanning tunneling microscopy (STM), because this is an issue with potential applications in many fields, such as molecular devices, biosensors, and crystal engineering.[1–8] In terms of adsorption strength, self-assemblies of molecules on solid surfaces may be divided into two groups: the chemisorbed self-assembly group, such as thiols on gold surfaces,[9] and the physisorbed self-assembly group, such as alkanes or their derivatives on highly oriented pyrolytic graphite (HOPG) surfaces.[2,10] Compared to chemisorbed self-assemblies, physisorbed molecules have more freedom to rotate and translate to achieve a desired structure, hence, physisorbed assemblies have attracted more and more attention in recent years.[3] Up to now, many controllable physisorbed self-assemblies have been studied.[3,10–16]

As a representative class of physisorbed systems, SAMs of alkanes have been intensively studied on HOPG, MoS_2, and gold surfaces.[2,10,17–22] In comparison to alkanes, alkanol molecules, terminating with OH groups at one end, may form additional hydrogen bonds, possibly influencing the structure of their self-assembled monolayers. Previously reported studies mainly focus on the self-assembly of alkanol molecules on HOPG surfaces.[23–25] Only a few reports deal with alkanol SAMs on other substrates, for example, a metal substrate, which may offer more potential applications.[26] Only one report of the self-assembly of 1-decanol at a liquid/Au(111) interface was reported in 1992 by Yeo et al.[26] It was claimed that 1-decanol molecules stood on their ends with the OH polar groups facing the gold substrates.

Here, we present the first systematic study of self-assemblies of alkanols (from 1-decanol to 1-triacontanol, 1-

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[a] H.-M. Zhang, Dr. J.-W. Yan, Prof. Dr. Z.-X. Xie, Prof. Dr. B.-W. Mao, Prof. Dr. X. Xu
State Key Laboratory of Physical Chemistry of Solid Surfaces
Department of Chemistry, Xiamen University
Xiamen 361005 (China)
Fax: (+86) 592-218-3047
E-mail: zxxie@xmu.edu.cn
xinxu@xmu.edu.cn

$C_NH_{2N+1}OH$, $N=10$–30) on Au(111) surfaces. All alkanol molecules were found to lie flat on the surface with the carbon-chain skeletons parallel to the Au(111) surface. This result is different from previously reported SAM structures of 1-decanol on Au(111) surfaces.[26] We propose structural models to explore the bonding mechanism and packing of alkanols on a Au(111) surface. As compared to alkanes, for alkanols we conclude that hydrogen bonding among the terminal hydroxy groups competes with the adsorbate–substrate interactions and the adsorbate–adsorbate interactions among the aliphatic chains, leading to the unique bonding features of the alkanol SAMs on the Au(111) surfaces.

Results and Discussion

Self-assembly of alkanols on Au(111) surfaces from 1-decanol to 1-triacontanol: Figure 1 shows typical STM images of alkanols on a reconstructed Au(111) surface. Figure 1a, b, d, f, g, i, and j display images of alkanols with an even number of carbon atoms (hereafter referred to as the even alkanols) from $N=10$ to 22, in which N refers to the number of carbon atoms in an alkanol molecule. The STM image of 1-triacontanol ($N=30$) is shown in Figure 1k as a representation of long-carbon-chain alkanols. For alkanols with an odd number of carbon atoms (hereafter referred to as the odd alkanols), the STM images of SAMs of 1-tridecanol ($N=13$), 1-pentadecanol ($N=15$), and 1-nonadecanol ($N=19$) are presented as examples (see Figure 1c, e, and h). As shown in Figure 1, superimposed lamellar structures are

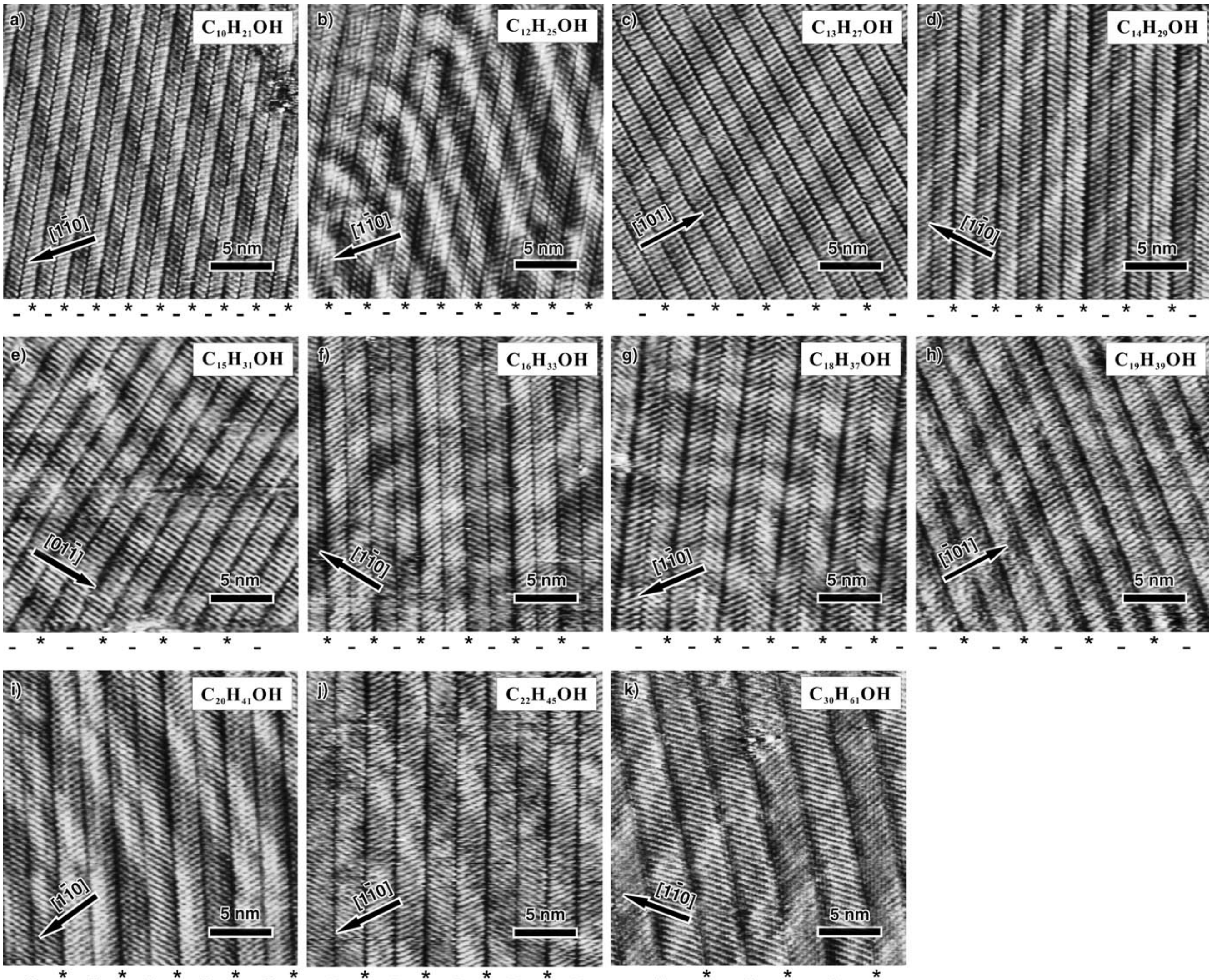

Figure 1. STM images of the self-assembled alkanols on reconstructed Au(111) surfaces. Images a), b), d), f), g), i), and j) display well-organized structures of alkanols with an even number of carbon atoms, from $N=10$ to 22. Image k) is an image of 1-$C_{30}H_{61}OH$ and is representative of long-chain alkanols with even N. Images c), e), and h) show SAMs of 1-$C_{13}H_{27}OH$, 1-$C_{15}H_{31}OH$, and 1-$C_{19}H_{39}OH$, respectively, and are representative of odd alkanols. The asterisks mark the troughs that are composed of alkanol functional groups, while the minus signs mark the troughs that are made up of CH_3 terminal groups. All images are 25 nm × 25 nm in area. The typical tunneling conditions are sample bias voltage (V_b) = 0.05 V and tunneling current (I_t) = 1.0 nA.

found on the reconstructed Au(111) surfaces and typical reconstruction ridges can be identified. Every lamella is composed of close-packed rods. The length of each rod is consistent with the length of an alkanol molecule. Therefore, a rod in the lamella is considered to be an individual alkanol molecule, lying flat on the surface in an all-*trans* conformation. This finding is in line with previous experimental observations for alkanols on HOPG and MoS_2 surfaces, and alkanes on reconstructed Au(111) surfaces.[21–25]

By carefully investigating the images, we find that the contrasts of lamellar troughs change alternately, in which the darker troughs are denoted by "*" and the less-dark troughs by "−" as shown in Figure 1. It has been established that the OH groups in alkanol SAMs on HOPG surfaces exhibit a reduced tunneling probability compared to the rest of the molecular chain.[23–25] Therefore the darker troughs can be attributed to the hydrogen-bonding area of the OH groups.

From hundreds of STM images of alkanol SAMs on gold, three kinds of lamellar structures can be identified. These are the herringbone-like structure, the tilted structure, and the perpendicular structure, as shown in Figure 2a, b, and c, respectively. In the herringbone-like structure (Figure 2a), the orientation of the long axes of the alkanol molecules on both sides of the darker trough (marked with "*") is different, forming a V shape. Figure 2b and c exhibit the other two kinds of typical packing structures, in which the orientations of the long axes of the alkanol molecules are parallel to each other. Figure 2b corresponds to the tilted structure, in which the long axes of molecules are tilted to the lamellar boundaries, while Figure 2c corresponds to the perpendicular structure, in which the long axes of the molecules are perpendicular to the lamellar boundaries. We note that perpendicular lamellar structures can only be found in SAMs of odd alkanols, while both herringbone-like and tilted lamellar structures are typical structures for even alkanols.

Here we define the structural parameters of the unit cell in Figure 2a, in which a is the minimum distance between two like lamellar troughs, b is the intermolecular distance in the SAMs, and θ is a complementary angle between the molecular long axes of even alkanols and the lamellar troughs. We found that besides parameter a, which is directly related to the carbon-chain length, both parameters b and θ increase as the length of the carbon chain increases. Thus, as parameter a increases from 2.6 ± 0.1 nm for $C_{10}H_{21}OH$ to 3.9 ± 0.1 nm for $C_{16}H_{33}OH$ to 5.3 ± 0.2 nm for $C_{22}H_{45}OH$, and to 6.8 ± 0.2 nm for $C_{30}H_{61}OH$, parameter b steadily increases from 0.51 ± 0.02 nm for the shortest alkanol (C_{10}) to 0.54 ± 0.03 nm for the longest alkanol (C_{30}). This change in the parameters a and b is accompanied by an increase of 2θ from $51 \pm 2°$ for the shortest alkanol to $60 \pm 3°$ for the longest alkanol. Similar trends are observed for odd alkanols, although it has been found that parameter a (for C_{2N+1}) is slightly longer than that of its even neighbors (for C_{2N} or C_{2N+2}), whereas parameter b is slightly shorter. A detailed discussion of the packing structures will be given in the next section.

From Figure 1 we conclude that the alkanol molecules adsorb at the liquid/substrate interface with their carbon-chain skeletons parallel to the Au(111) surface. This conclusion contradicts that of a previous experiment.[26] In a report by Yeo et al.,[26] the alkanol SAM samples were prepared by applying pure 1-decanol liquid onto gold films, which were then left undisturbed for several hours. It was claimed that the 1-decanol molecules stand on their ends with the OH polar groups facing the gold substrate, and the presence of monolayers was strongly influenced by the tip polarity. We did not find any STM images of 1-decanol molecules with their molecular long axes perpendicular to the substrate under the same experimental conditions. Furthermore, the structure of the alkanol SAMs was not found to be influenced by the tip polarity during the STM observations.

Packing of alkanol molecules on reconstructed Au(111) surfaces: When molecules adsorbed on Au surfaces forming an incommensurate structure, with respect to the substrate

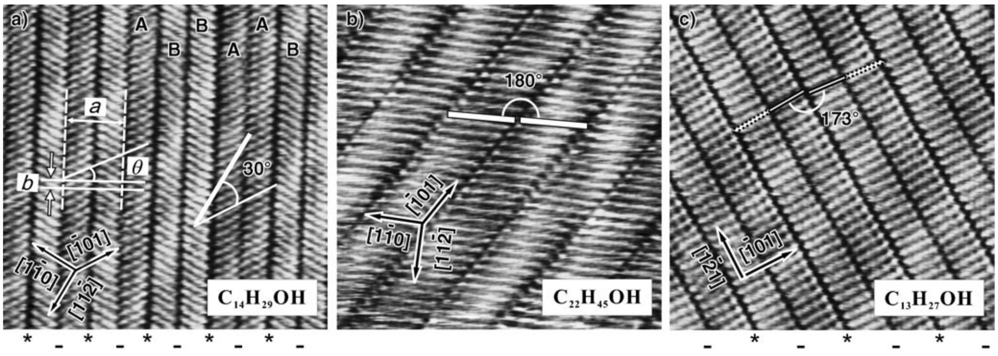

Figure 2. High-resolution STM images of three kinds of packing structures: a) the herringbone-like structure (1-$C_{14}H_{29}OH$, 20 nm × 20 nm), b) the tilted structure (1-$C_{22}H_{45}OH$, 15 nm × 15 nm), and c) the perpendicular structure (1-$C_{13}H_{27}OH$, 15 nm × 15 nm). In image (a) "*" marks the troughs that are composed of alkanol functional groups and "-" marks the troughs that are composed of CH_3 terminals. The **A** labels mark the lamellae in which the molecular axes are located in the [$\bar{1}$01] direction, and the **B** labels mark the lamellae in which the molecular axes are located in the [1$\bar{1}$0] direction. Image b) shows the tilted structure observed in SAMs of 1-docosanol. Image c) shows the perpendicular structures found in SAMs of 1-tridecanol, for which the angle between the long axes of the molecules in two adjacent lamellae diverges from a straight angle to a 173° angle.

structure, Moiré patterns usually appeared. The presence of these patters corresponds to the formation of superlattices of adsorbed layers on the substrate. In our experiments, we did not observe a Moiré pattern for SAMs of alkanols on a Au(111) surface, implying that the self-assembled monolayers are commensurate with respect to the Au(111) surface.

Figure 3 shows a schematic model of the reconstructed Au(111) surface (the uniaxial reconstructed surface), in which lattice shortening occurs on the surface along the $[1\bar{1}0]$ direction, such that the space originally for 22 Au atoms is occupied by 23 Au atoms. The periodicity of the reconstructed Au lattice is 0.50 nm along the $[11\bar{2}]$ direction, but the periodicity is reduced to 0.48 nm along the $[\bar{2}11]$ or $[1\bar{2}1]$ directions. Such reconstructed surfaces were found to be critical for the self-assembly of *n*-alkanes, to achieve optimized adsorbate–adsorbate interactions among the aliphatic chains and the adsorbate–substrate interactions.[21,22] However, for the alkanol molecules, the introduction of OH groups certainly influences the packing structures through the formation of hydrogen bonds.

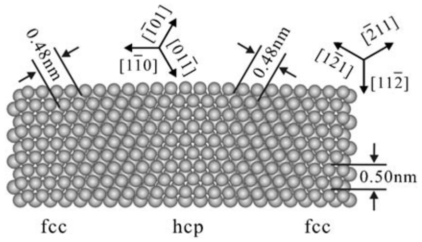

Figure 3. A schematic model of a reconstructed Au(111) surface.

For SAMs of even alkanols, the herringbone-like structure is typical, in which the alkanol molecules form a V shape along the hydrogen-bond troughs. The alkanol molecules on one side of the V-shaped structures were measured to be around 30° with respect to the Au(111) reconstruction ridges underneath (marked by **A** in Figure 2a), while the long axes of the alkanol molecules were perpendicular to the Au(111) reconstruction ridges on the opposite side (marked by **B** in Figure 2a). Therefore, we deduce that the alkanol molecules on lamella **A** were adsorbed along the $[\bar{1}01]$ direction of the Au(111) substrate, while the long axes of the molecules on lamella **B** were located along the $[1\bar{1}0]$ direction.

By measuring the intermolecular distance of molecules on lamellae **A** and **B** in Figure 2a, we found that the mean values of the intermolecular distances were 0.47 ± 0.01 nm in domain **A**, and 0.49 ± 0.01 nm in domain **B**. These correspond to the periodicities of the gold substrate along the $[1\bar{2}1]$ and $[11\bar{2}]$ directions. All these facts are consistent with the conclusion that the alkanol molecules are restricted in the gold-atom troughs forming commensurate monolayers with respect to the reconstructed Au(111) surfaces. Figure 4a shows a schematic model of the herringbone-like lamellae.

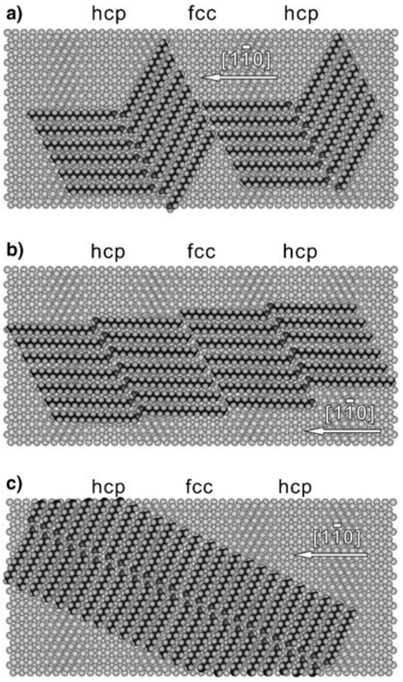

Figure 4. Packing models of alkanol molecules on reconstructed Au(111) surfaces: a) the herringbone-like packing of 1-docosanol molecules, b) the tilted packing structures of 1-docosanol molecules, and c) the perpendicular packing structures of 1-pentadecanol molecules.

For alkanol SAMs with tilted structures, shown in Figure 2b, the angle between two molecular axes in adjacent lamellae is about 180°. Such tilted structures, although dominant in SAMs of the alkanes, appear with less possibility than the herringbone-like structures in SAMs of the even alkanols. In the tilted monolayers, alkanol molecules usually lie perpendicular to the gold reconstructed ridges, so that molecules are adsorbed in the gold atom troughs along the $[1\bar{1}0]$ direction. The intermolecular distance within the lamellae was measured to be 0.50 ± 0.02 nm, which is consistent with the periodicity of the gold surface along the $[11\bar{2}]$ direction. Figure 4b shows a schematic model of the tilted lamellae. Recall that alkane molecules prefer $[01\bar{1}]$ or $[\bar{1}01]$ directions with a periodicity of 0.48 nm, instead of the $[1\bar{1}0]$ direction, to achieve the optimized adsorbate–adsorbate and adsorbate–substrate interactions. Thus, the observed preference for alkanol molecules along the $[1\bar{1}0]$ direction must originate from the preferential hydrogen bonding observed along this direction.

In SAMs of the perpendicular structures, which are typical structures for the odd alkanols, the alkanol molecules were found to locate along the $[\bar{1}01]$ direction (see Figure 2c). The long axes of the alkanol molecules lie at an angle of around 30° with respect to the Au(111) reconstruction ridges, rather than perpendicular to the ridges. The measured intermolecular distance in SAMs of 1-tridecanol ($N=13$) is 0.48 ± 0.01 nm, which corresponds to the periodic distance of the gold atom troughs along the $[1\bar{2}1]$ direction, supporting the conclusion that molecules are adsorbed in the gold-atom troughs along the [$\bar{1}01$] direction. A schematic model of the perpendicular structure is shown in Figure 4c.

Influence of substrate–adsorbate and adsorbate–adsorbate interactions on the packing of alkanol molecules on Au(111) surfaces: For even alkanols, two kinds of packing structures are observed: the herringbone-like structure and the tilted structure. The packing structures were found to be sensitive to the length of the carbon chain. At room temperature, only the herringbone-like structures were found on reconstructed Au(111) surfaces for $N<18$. Tilted lamellae first appeared when $N=18$, although the herringbone-like structures still dominated. Figure 5a and b show SAMs of $C_{18}H_{37}OH$ and $C_{20}H_{41}OH$ on the reconstructed Au(111) surfaces, in which the coexistence of the herringbone-like and tilted structures can easily be seen. With an increasing number of carbon atoms, the probability of forming tilted structures increases. Figure 5c shows that tilted lamellae prevailed in some areas of 1-docosanol SAMs ($N=22$) on reconstructed Au(111) surfaces.

The structures of alkanol SAMs depend on a subtle balance between the adsorbate–substrate and adsorbate–adsorbate interactions. The latter involves not only the aliphatic chain interactions, which are common in both alkanol and alkane SAMs, but also the hydrogen-bonding interactions, which are unique in the alkanol SAMs. For long-chain alkanols, it is reasonable to anticipate that the alkanols resemble alkanes in the formation of SAMs, as the aliphatic chain interactions make a greater contribution, whereas for short-chain alkanols, hydrogen bonding is expected to play a critical role. Figure 6 depicts some molecular details of the hydrogen-bonding interactions in a) the herringbone-like structure, b) the titled structure, and c) the perpendicular structure. Although the OH groups are in the dark parts of the STM images, these pictures are based on theoretical predictions by using molecular mechanics for 1-octadecanol ($N=18$) on HOPG surfaces. The degree of stability follows the trend a) > b) ≫ c).[27] It has been concluded that the hydrogen-bonding interactions drive the intermolecular-packing geometry of the herringbone-like structures of alkanol overlays, with an angle of around 130°.[25] This may explain why the V-shaped lamellae are dominant for the even alkanols on Au(111) surfaces. To obtain an optimized adsorbate–substrate interaction for long-chain alkanols, the alkanol molecules must adsorb along the gold-atom troughs, for example, along the [$1\bar{1}0$] and [$\bar{1}01$] troughs, with an angle of about 120°. This commensurate structure is achieved at the expense of hydrogen bonding. By carefully measuring the

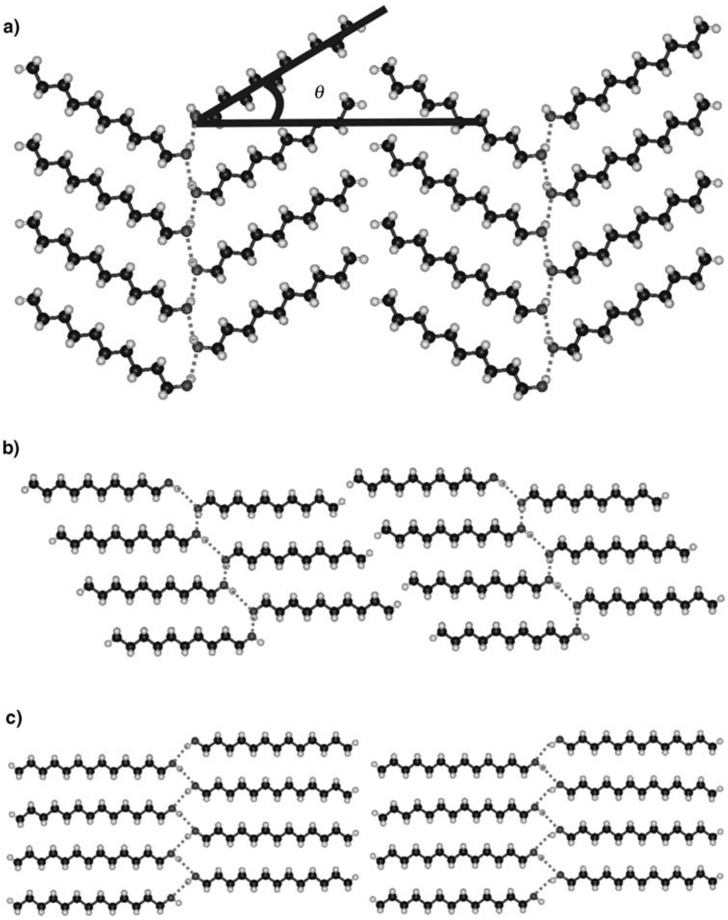

Figure 6. Hydrogen-bonding models of: a) the herringbone-like packing of 1-decanol molecules, b) the tilted packing structures of 1-decanol molecules, and c) the perpendicular packing structures of 1-tridecanol molecules.

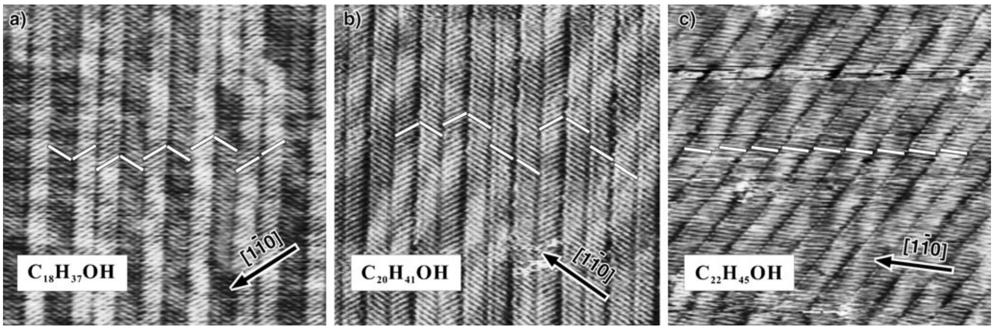

Figure 5. Dependence of the packing structures on the carbon-chain length for even alkanols on reconstructed Au(111) surfaces. STM images of SAMs of a) 1-$C_{18}H_{37}OH$, b) 1-$C_{20}H_{41}OH$, and c) 1-$C_{22}H_{45}OH$ at room temperature, showing that an increase of the carbon-chain length favors tilted structures. White bars marked on the images represent alkanol molecules. All STM images are 30 nm × 30 nm in area.

angle θ as shown in Figure 6a, we obtained values of 25, 27, and 29° for decanol ($N=10$), tetradecanol ($N=14$), and docosanol ($N=22$), respectively. Thus, the molecular-axes angle between molecules on both sides of a dark trough were 130, 126, and 122° for decanol, tetradecanol, and docosanol, respectively; these values gradually approach an ideal value of 120° for the substrate geometry (from an optimized angle for hydrogen bonding of 130°) with increasing chain length of the alkanol molecules. In fact, similar phenomena were also found for the V-shaped lamellae of the alkanol SAMs on HOPG surfaces,[25] in which the angles between the molecular axes were 134, 132, and 130° for decanol, dodecanol, and tetradecanol, respectively.

A previous study on the self-assembly of a mixture of triacontanol and triacontane ($N=30$) on HOPG surfaces revealed that domains of both the alkane and the alkanol SAMs were formed and coexisted on the graphite surfaces.[24] This may indicate that triacontanol behaves similarly to triacontane on HOPG surfaces, with a comparable net bonding strength when both the adsorbate–adsorbate interactions and adsorbate–substrate interactions are taken into consideration. Therefore, it is reasonable to expect that long-chain alkanol SAMs may adopt the structures of alkane SAMs. Recalling that the tilted lamellar structure is typical for alkane SAMs, a strong adsorbate–substrate interaction may make the tilted lamellar structure favorable, transforming the herringbone-like to a tilted structure. A similar transformation was also observed for octadecanamide on graphite and MoS_2 surfaces through rotation about the C−C bond adjacent to the amide group.[28]

Experiments carried out measuring the surface excess mass of hydrocarbons on graphite provided further support for the theory that alkanol SAMs exhibit more characteristics of the aliphatic chains when $N>18$.[29] Findenegg found that for $N<18$ an alkanol molecule possesses a higher surface excess mass than an alkane of the same chain length. The additional stabilization of the alkanols arises from the hydrogen-bonding interactions formed between OH groups of neighboring molecules. When the number of carbon atoms was 18 or greater, the surface excess mass of alkanol was found to be the same as that of an alkane molecule of the same chain length. Therefore, alkanols are more like alkanes in SAM formations in which $N\geq 18$.

It is worthwhile emphasizing the difference between even alkane SAMs and the even alkanols. While both tilted and perpendicular structures can be seen, the herringbone-like structures are rarely observed in SAMs of even alkanes on reconstructed Au(111) surfaces. On the other hand, while herringbone-like structures dominate in short-chain alkanols, which may transform to tilted structures with an increase of the carbon-chain length, perpendicular structures are rarely observed for even alkanols. Furthermore, the tilted structures of alkanols differ from those of alkanes. While the alkanol molecules align along the $[1\bar{1}0]$ direction, the alkane molecules allign along the $[\bar{1}01]$ direction. These differences must be related to a subtle balance between the adsorbate–substrate and adsorbate–adsorbate interactions, in which hydrogen bonding plays an additional and critical role in alkanol SAMs.

For the odd alkanols, the typical structure observed is the perpendicular structure, in which the molecular axes are perpendicular to lamellar troughs and the molecules in adjacent lamellae are staggered by half of the molecular width (see Figure 1c, e, h, and Figure 2c). When perpendicular structures were formed, the lamellar troughs were always found to lie along the $\langle 112\rangle$ directions, which are the next nearest neighboring (NNN) directions, and the molecular axes were always oriented in the $\langle 110\rangle$ directions, which are the nearest neighboring (NN) directions. This is the same result as that observed in SAMs of odd alkanes on Au(111) surfaces.[19,22] Hence, as pointed out by Uosaki and co-workers and Zhang et al., the perpendicular structures are determined by the directions of the terminal CH_3 groups of the odd-numbered carbon chains.[19,22]

As expected, hydrogen bonding also affects the detailed lamellar structures. By careful investigation of the high-resolution STM images of 1-tridecanol ($N=13$) (Figure 2c), we found that molecules between two adjacent lamellae diverged from parallel directions. The measured angle of the molecular long axes between two adjacent lamellae is about 173°. This value may be compared to the straight angle found in SAMs of *n*-tridecane and other odd alkanes.[19,22] Such a divergence in molecular orientation is attributed to the hydrogen-bonding effect, in which tridecanol molecules rotate slightly to achieve better hydrogen-bonding interactions. With an increase of the carbon-chain length, alkanol molecules should be gradually restricted in the gold-atom troughs to maximize adsorbate–substrate bonding. In fact, nonadecanol molecules ($N=19$) between two adjacent lamellae in Figure 1h are found to be in a close parallel configuration.

Self-assembly of alkanol molecules on unreconstructed Au(111) surfaces: It was found that normal alkanes can only self-assemble on unreconstructed Au(111) surfaces with the help of an external force, such as an electric field, at room temperature.[22] For normal alkanols, however, SAMs are formed on unreconstructed Au(111) surfaces, as shown in Figure 6. No reconstructed ridges can be found in the STM images, in which a, b, and c clearly show SAMs of 1-dodecanol, 1-octadecanol, and 1-docosanol, respectively. The geometric parameters for the unit cell of SAMs on the unreconstructed Au(111) surfaces were found to be very similar to those on reconstructed surfaces.

As discussed in our previous papers,[22] the reconstructed Au(111) surfaces provide shortened gold troughs (with about 0.48 nm in periodicity) along two directions. The alkane molecules were found to only adsorb along these two directions, in which SAMs gained maximum intermolecular interactions by forming a commensurate structure. However, for unreconstructed Au(111) surfaces, the corresponding periodicity of gold troughs is about 0.50 nm in all three directions, making a commensurate structure unachievable. As a result, the alkane molecules do not form SAMs on unrecon-

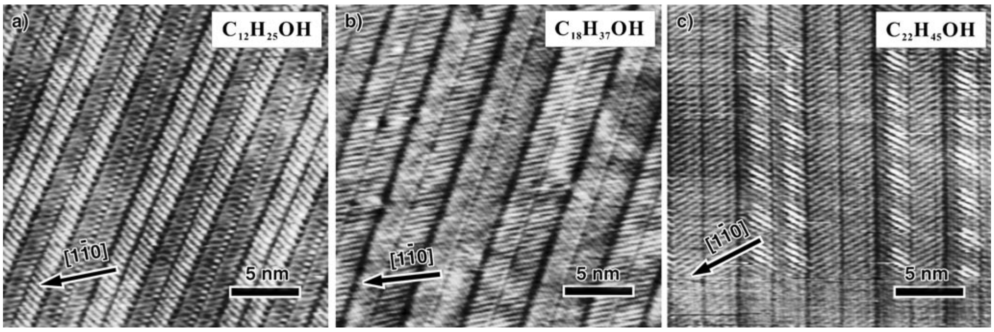

Figure 7. Self-assembled monolayers of alkanols on unreconstructed Au(111) surfaces. STM images of a) 1-dodecanol, b) 1-octadecanol, and c) 1-docosanol.

structed Au(111) surfaces without the help of any other external force to re-establish the balance between the adsorbate–adsorbate and adsorbate–substrate interactions. In comparison to alkane molecules, alkanol molecules increase the adsorbate–adsorbate interactions significantly in the self-assembled monolayers by forming hydrogen-bonded chains. We believe that it is this additional hydrogen bonding that allows the formation of SAMs of alkanols on unreconstructed Au(111) surfaces (see Figure 7)

Conclusion

A systematic study of self-assembled monolayers of alkanol molecules with different chain lengths (from 1-decanol to 1-triacontanol, 1-$C_NH_{2N+1}OH$, $N=10$–30) on Au(111) surfaces has been performed. The main conclusions are:

1) Normal alkanols form well-ordered monolayers with the carbon-chain skeletons parallel to the Au(111) surfaces. This result is different from an earlier report, which claimed that 1-decanol molecules stood on their ends with the OH polar groups facing the gold substrate.
2) Being different from the self-assemblies of normal alkanes, normal alkanols can form self-assembled monolayers either on reconstructed or unreconstructed Au(111) surfaces. Hydrogen-bonding interactions in alkanols provide extra bonding features, so that the even alkanol molecules allign along the $[1\bar{1}0]$ direction, while the even alkane molecules allign along the $[\bar{1}01]$ direction.
3) At room temperature (ca. 25 °C), the packing structures for SAMs of odd and even alkanols are different. For even alkanols, SAMs assume a herringbone-like structure for $N<18$ and may transform to a tilted structure for $N\geq 18$. For odd alkanols, the perpendicular structure is the most typical structure.

Experimental Section

Reconstructed Au(111) surfaces of a single-crystalline bead fixed on a Au sheet were prepared by Clavilier's method,[30] followed by careful annealing in a hydrogen flame. 1-Tridecanol (1-$C_{13}H_{27}OH$, Lancaster, 98%), 1-tetradecanol (1-$C_{14}H_{29}OH$, Acros, 99%), 1-pentadecanol (1-$C_{15}H_{31}OH$, Acros, 99%), 1-hexadecanol (1-$C_{16}H_{33}OH$, Avocado, 99%), 1-octadecanol (1-$C_{18}H_{37}OH$, TCI, 99%), 1-nonadecanol (1-$C_{19}H_{39}OH$, Aldrich, 99%), 1-eicosanol (1-$C_{20}H_{41}OH$, Acros, 98%), 1-docosanol (1-$C_{22}H_{45}OH$, Sigma, 99%), and 1-triacontanol (1-$C_{30}H_{61}OH$, Sigma, 99%) were dissolved in *n*-tetradecane (*n*-$C_{14}H_{30}$, Fluka, 99%) to produce saturated solutions at room temperature. For 1-decanol (1-$C_{10}H_{21}OH$, Avocado, 99%) and 1-dodecanol (1-$C_{12}H_{25}OH$, Fluka, 99.5%), we used the neat liquid directly. All of these chemicals were used without further purification. After putting a droplet of the alkanol solution or the alkanol neat liquid on a freshly annealed Au(111) surface, a mechanically sharpened Pt/Ir tip was immersed in the solution to enable STM analysis (Nanoscope IIIa, Digital Instrument) at room temperature. Typically a 100 mV bias voltage and 1.0 nA tunneling current were used for recording images.

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