Communications

Structural Investigation of 4-Methylbenzenethiol Self-Assembled Monolayers on Au(111) by Scanning Tunneling Microscopy

Hungu Kang and Jaegeun Noh*

Department of Chemistry and Institute of Nano Science and Technology, Hanyang University, Seoul 133-791, Korea
*E-mail: jgnoh@hanyang.ac.kr
*Received January 10, 2014, Accepted January 22, 2014*

Self-assembled Monolayers (SAMs) Formed by the Spontaneous Adsorption of Organic Thiols on Metal Surfaces offer a powerful route for potential applications in a variety of fields such as corrosion inhibition, lubrication, sensors, biointerface, and nanopatterning.[1-4] Recently, SAMs of aromatic thiols have drawn considerable attention due to their practical applications in molecular electronic devices.[5,6] It has been demonstrated that the work function of metal electrodes in electronic devices can be easily tuned by introducing the SAMs of ω-functionalized aromatic thiols with different functional group[5-8] and the performance of SAM-modified devices was strongly dependent on the molecular orientation of adsorbed molecules.[8] Therefore, it is essential to understand the surface structure and molecular orientation of aromatic thiol SAMs as well as to control two-dimensional (2D) structure of SAMs for the development of electronic devices. Structural order of aromatic thiol SAMs on Au(111) was considerably enhanced by increasing the number of phenyl ring in the molecular backbone[9-11] and by inserting the alkyl spacer between the phenyl ring and the sulfur atom.[12,13] High-resolution scanning tunneling microscopy (STM) imaging revealed that the adsorption of benzenethiol (BT) on Au(111) at 50 °C led to the formation of well-ordered SAMs showing the $(2 \times 3\sqrt{2})R30°$ structure,[9,12] while fluorinated benzenethiol SAMs have quite different packing strcutures.[14,15] So far, numerous reports have mainly focused

on the surface structure, molecular orientation, self-assembled process and physical property of SAMs formed by various aromatic thiols.[6-16] However, there have been very few reports on the structure and orientation of SAMs of 4-alkylbenzenethiols with a nonpolar sustituent.[17]

The main purpose of this work is to elucidate how much the alkyl substituent of benzenethiol at 4-position affects the formation and structure of SAMs. To explore this question, we examined 4-methylbenzenethiol (4-MBT) SAMs prepared in a 1 mM ethanol solution using STM, and revealed for the first time that 4-MBP molecules on Au(111) at 75 ºC form 2D ordered SAMs describing a $(2\sqrt{3} \times \sqrt{11.5})R30°$ structure.

Atomically flat Au(111) substrates were prepared by thermal evaporation of gold onto mica as described previously.[10] 4-MBT SAMs were prepared by dipping the Au(111) substrate in a 1 mM ethanol solution of 4-MBT at room temperature or 75 °C for 2 h. STM measurements were carried out using a NanoScope E (Veeco, Santa Barbara, CA) with a commercial Pt/Ir (80:20) tip under ambient conditions. Imaging parameters were in the range of 300-500 mV for the bias voltage and in the range of 0.30-0.60 nA for the tunneling current between the tip and the sample.

STM images in Figure 1 show the surface structures of 4-MBT SAMs on Au(111) formed after immersion in a 1 mM ethanol solution at room temperature and 75 °C for 2 h. The adsorption of 4-MBT molecules on Au(111) at room temperature yielded to the disordered SAMs containing gold adatom islands (bright spots), as shown in Figure 1(a). The similar structure was often observed for other aromatic thiol SAMs.[9,10,12,15] It was suggested that the formation of gold adatom islands is due to a low mobility of gold adatoms emerged from the first gold layer during the chemisorption of aromatic thiols on gold surfaces. Therefore, higher deposition temperature can increase a mobility of gold adatoms and a diffusion rate of adsorbing molecules on the gold surfaces, resulting in the formation of high quality SAMs with a structural order and without such gold a datom islands. For instance, the adsorption of BTs,[16] pentafluorobenzene-
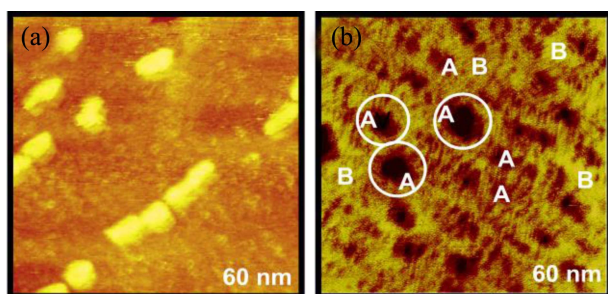

Figure 1. STM images of 4-MBT SAMs on Au(111) formed after immersion in a 1 mM ethanol solution at (a) room temperature and (b) 75 °C for 2 h.

thiols,[15] and terphenylthiols[11] on Au(111) at an elevated solution temperature would form well-ordered

SAMs without any adatom islands. In this work, we also found that 2D ordered 4-MBT SAMs were formed when adsorption occurred at 75 °C, as shown in Figure 1(b). The ordered phases were formed on an entire gold surface and composed of two different domains (indicated by A and B). Imaging contrast of region A is slightly darker than that of region B, which may be due to a difference in adsorption geometry of 4-MBT in the SAMs. It is reasonable to assume that the molecular backbones of 4-MBTs in the dark region are more tilted to the surface compared to those in the bright region. Interestingly, this suggestion can be strongly supported from the fact that a number of A regions were located around vacancy islands (dark holes, VIs), indicated by the white circles. In fact, the formation of closely packed SAMs with standing-up adsorption geometry is rather difficult around VI regions because of low van der Waals interactions between molecular backbones.

STM image in Figure 2(a) clearly shows the ordered molecular rows of 4-MBT SAMs on Au(111) in the dark and bright regions. The 2D fast Fourier transform (FFT) filtered STM image in Figure 2(b) shows the individual molecules in the ordered rows from the area of rectangular box on the image of Figure 2(a). On the basis of this STM observation, we extracted the lattice constants of an oblique unit cell containing four molecules: $a = 10.0 \pm 0.2$ Å $= 2\sqrt{3}a_h$ and $b = 9.8 \pm 0.2$ Å $= \sqrt{11.5}a_h$, where $a_h = 2.89$ Å and represents the interatomic distance of the Au(111) lattice. The molecular packing structure for 4-MBT SAMs can be referred to as a $(2\sqrt{3} \times \sqrt{11.5})R30°$ structure, which is comparable to the previously observed structures: $4 \times \sqrt{3}$ and $2\sqrt{3} \times \sqrt{3}$ structures.[17] This structural discrepancy between our and their results is due to different SAM preparation conditions because they prepared SAMs in a 0.05 mM ethanol solution at RT for 5 min and STM observation was performed under electrochemical environments (0.1 M $HClO_4$ at 0.4 V). On the other hand, the surface structures of 4-MBT SAMs with a nonpolar substituent were completely different from those of fluorobenzenethiol (4-FBT) SAMs with a polar substituent even if 4-FBT SAMs were prepared using same preparation conditions.[13] 4-MBT SAMs have ordered phases on an entire gold surface, whereas 4-FBT SAMs contained disordered phases containing a small ordered domain. From this work, it is clear that the formation of poorly ordered phase for 4-FBT SAMs on Au(111) results from the repulsion of molecular dipole moment between molecular backbones in the SAMs. We consider that the formation of unique ordered domains for 4-MBT SAMs is mainly driven by the π-π interactions between the benzene rings and is influenced by the terminal methyl groups during self-assembly.

In summary, we demonstrated that the adsorption of 4-
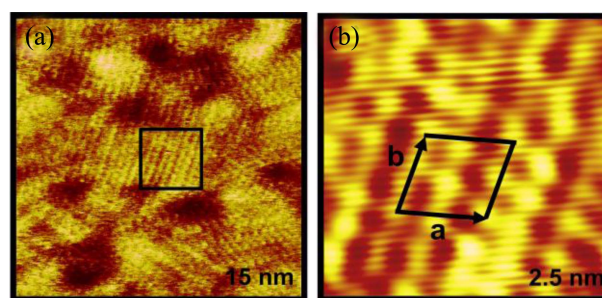
Figure 2. (a) STM image ordered 4-MBT SAMs on Au(111) in a 1 mM ethanol solution at 75 °C for 2 h. (2) 2D FFT filtered STM image of rectangular box on STM image 2a.

MBTs on Au(111) at 75 ºC for 2h led to the formation 2D ordered SAMs describing a $(23 \times \sqrt{11.5})R30°$ structure. Our results obtained here will be very useful for understanding the formation and surface structures of 4-MBT SAMs on Au(111) surfaces.

References

1. Love, J. C.; Estroff. L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103.
2. Lee, N.-S.; Kim, D.; Kang, H.; Park, D. K.; Han, S. H.; Noh, J. *J. Phys. Chem. C* **2011**, *115*, 5868.
3. Ito, E.; Ito, H.; Kang, H.; Hayashi, T.; Hara, M.; Noh, J. *J. Phys. Chem. C* **2012**, *116*, 17586.
4. Kang, H. Noh, J. *Bull. Korean Chem. Soc.* **2013**, *34*, 1383.
5. Lim, J. A.; Lee, H. S.; Lee, W. H.; Cho, K. *Adv. Funct. Mater.* **2009**, *19*, 1515.
6. Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791.
7. Hong, J.-P.; Park, A.-Y.; Lee, S.; Kang, J.; Shin, N.; Yoon, D. Y. *Appl. Phys. Lett.* **2008**, *92*, 143311.
8. Schmidt, C.; Witt, A.; Witte, G. *J. Phys. Chem. A* **2011**, *115*, 7234.
9. Dhirani, A. A.; Zehner, R. W.; Hsung, R. P.; Guyot-Sionnest, P.; Sita, L. R. *J. Am. Chem. B* **1996**, *118*, 3319.
10. Kang, H.; Shin, D. G.; Han, J. W.; Ito, E.; Hara, M.; Noh, J. *J. Nanosci. Nanotech.* **2012**, *12*, 557.
11. Bashir, A.; Azzam, W.; Rohwerder, M.; Terfort, A. *Langmuir* **2013**, *29*, 13449.
12. Noh, J.; Ito, E.; Hara, M. *J. Colloid Interf. Sci.* **2010**, *342*, 513.
13. Kang, H.; Lee, S.; Ito, E.; Hara, M.; Noh, J. *J. Nanosci. Nanotech.* **2012**, *12*, 4274.
14. Jiang, P.; Deng, K.; Fchou, D.; Xie, S.-S.; Nion, A.; Wang, C. *Langmuir* **2009**, *25*, 5019.
15. Kang, H.; Lee, S.; Ito, E.; Hara, M.; Noh, J. *Langmuir* **2010**, *26*, 2983.
16. Kang, H.; Park, T.; Choi, I.; Lee, Y.; Ito, E.; Hara, M.; Noh, J. *Utramicroscopy* **2009**, *109*, 1011.
17. Seo, K.; Borguet, E. *J. Phys. Chem. C* **2007**, *111*, 6335.