

Adsorption and EUV-Induced Modification of Furoxanethiols for Diverse Functionalities on Gold Surface

Hyun Seo Koo, Han-Na Hwang,[‡] Yoon Man Lee, Joon Won Park,[†] Chan-Cuk Hwang,^{*,‡} and Kwang-Jin Hwang^{*}

Department of Bio & Chemical System Engineering, Hongik University, Sejong 339-701, Korea. *E-mail: kjhwang@hongik.ac.kr

[†]Department of Chemistry, Division of Integrative Biosciences and Biotechnology, WCU Program, Pohang University of Science and Technology, Pohang 790-784, Korea

[‡]Pohang Accelerator Laboratory, Pohang 790-784, Korea. *E-mail: cchwang@postech.ac.kr

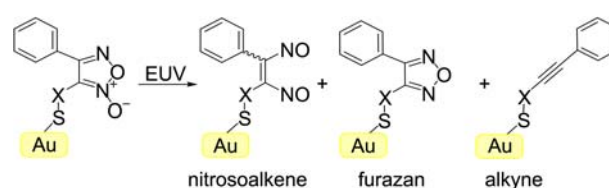
Received July 12, 2012, Accepted September 17, 2012

Key Words : Furoxanethiol, Ring-opening, Furazan, Alkyne

Site selective conversion of self-assembled molecular films into reactive functional groups has attracted considerable interest, as the resultant materials can be widely applied to areas including bio chips, diagnostic nanoarrays, and molecular assembly patterning.¹ Regarding studies to form reactive functionalities by the functional group modifications on self-assembled thin films, the following approaches have been reported: nitroaldimine reduction and amine formation by soft X-rays or electronic beams,^{2,3} thiol formation by electric reduction of thiocarbamate,⁴ alkane oxide formation by oxidative photolysis of alkane,⁵ photochemical cross-linking of biphenyl thiol,⁶ triazole formation,⁷ and photon or electron mediated alkyne formation from the furoxan.^{8,9}

With respect to patterning of molecular layers on a material surface, photochemical conversion is considered as one of the best techniques to obtain arrayed functionalities on a solid surface. For the photochemical generation of functional groups on self-assembled monolayers (SAMs), especially in a patterned manner, the selection of photosensitive molecules consisting of SAMs is considered essential. The molecules should maintain stable molecular assembly states, and should also be sensitive to light-irradiation in order to afford new functional groups that can initiate subsequent functional modifications for adequate surface patterning.

Furoxan (furazan *N*-oxide) compounds are known to be the only potential alkyne precursor that can generate triple bonds on solid phases by photochemical conversions.⁸⁻¹¹ In our previous studies regarding the alkyne formation from furoxans on silica, however, imine bonding between furoxan-aldehyde and an amino group on the silica surface limited its wide application because of air-instability-induced decomposition and a reductive response with the irradiating light.^{2,9} Thus, furoxanethiols PFT and BPFT were deposited on gold



Scheme 1. Proposed structures derived from furoxan derivatives upon EUV irradiation on gold (X = CH₂ for PFT, X = C₆H₄CH₂ for BPFT).

surfaces and then exposed to EUV (Extreme Ultra Visible) in order to fabricate stable furoxan thin-film *via* simpler methods and examine the photo-reactivity of furoxan derivatives. Since amino linkers were not used in the process for making furoxan thin films on gold surface, XPS analysis of nitrogen atoms could be processed more clearly. We observed that the furoxanethiols showed different adsorption properties on the gold surface and different response upon EUV irradiation generating dinitrosoalkene and furazan functional groups together with alkyne on the gold surface (Scheme 1), in contrast with results obtained on silica.

Furoxan compounds PFT and BPFT were vapor deposited on gold and the resulting thin films were irradiated by EUV. HRPES (High Resolution Photoemission Spectroscopy) data for furoxans on gold surfaces before and after irradiation are presented in Figure 2. Shown are surface-sensitive N 1s core level spectra of the furoxans thin film after taken with photon energy of 470 eV. The dots are measured spectra and the solid curves are fitting results. The N 1s spectrum was fitted with two components using Gaussian width of 1.5-1.7 eV and Lorentzian width of 0.2-0.25 eV. The binding energies of the N1 and N2 components are 405.2 and 401.2 eV, respectively. The N1 component is attributed to the N(2) nitrogen bonded to two oxygens (O-N⁺-O), and N2 is for N(5) bonded to one oxygen (C=N-O) in a furoxan ring.

Considering the chemical environment of the PFT molecules, the intensity ratio between N1 and N2 components should be 1:1 in Figure 2(a). However, given that the two peak intensity ratios are not the same and that the number of N2 components is relatively larger, it is assumed that furo-

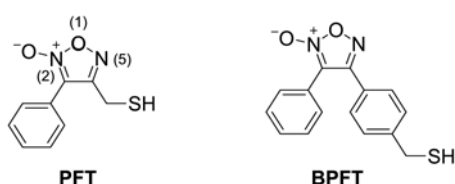


Figure 1. Structure and abbreviation of furoxanthiol derivatives.

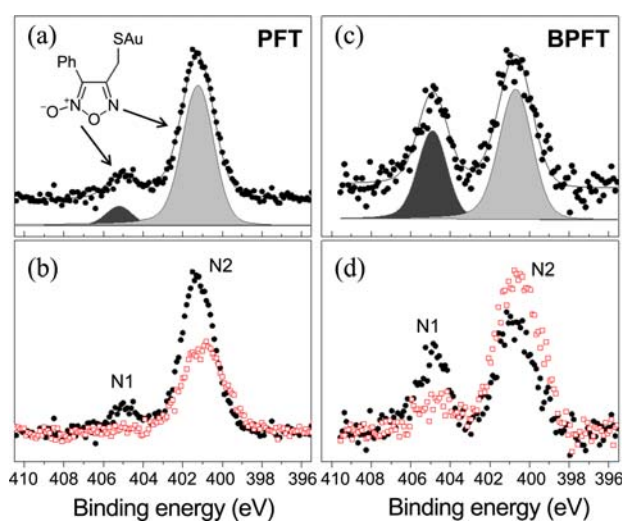


Figure 2. N 1s core level spectra of **PFT** (a, b) and **BPFT** (c, d). Fitting results for the samples before irradiation are presented in (a) and (c). Comparison of data before (black filled circle dot) and after (red open square dot) irradiation with EUV (92.5 eV) (b and d).

xan **PFT** is absorbed onto gold in diverse forms during the process of adsorption. It appears that the ring structure of furoxan ($-\text{O}-\text{N}^+-\text{O}$) was altered through interactions with gold,¹³ resulting in much more nitrogen atoms being coupled with only one oxygen atom. Based on the fragmentation mechanism of furoxans in gas or solution phase,^{10,11,14} it is assumed that the additional N2 component is attributed to the dinitrosoalkene or the furazan originating from the ring-opening and the deoxygenation reactions, respectively (Scheme 1).

The N 1s core level spectrum (red) of **PFT** obtained after irradiation with EUV (92.5 eV) is shown in Figure 2(b) together with the spectrum obtained before irradiation (black). After irradiation, the N1 peak completely disappeared and the N2 peak was reduced. The decrease in the N1 component ($-\text{O}-\text{N}^+-\text{O}$) together with N2 was considered to be the result of the progression of NO release from **PFT** by EUV. Indeed, a slight decrease in the O 1s core level spectrum was also observed after irradiation (not presented here). However, contrary to our expectation, the amount of reduction in the N2 peak was much larger than the reduction in the N1 peak. This result implies that NO was not only directly released from furoxan rings, but also additionally released from the dinitrosoalkene that previously formed during adsorption.

The reason that most N2 component and oxygen atoms remain even after EUV irradiation may be related to furazan formation. Furazan, a 5-membered heterocyclic, is known to be quite stable in various chemical environments due to its aromaticity.¹⁵ Thus, the deoxygenation of **PFT** might take place in the stage of adsorption or in the process of irradiation, leading to furazan formation on a gold surface while retaining the aromaticity. The facile deoxygenation of furoxans on the gold surface could be attributed to the Lewis acid interactions of gold with oxygen.^{13,16} Furthermore, the N2 peak broadened after the photoreaction of **PFT**. It is likely that there are nitrogen atoms with slightly different chemical

environments produced by unidentified reaction products such as trimembered azirine-oxide^{11,17} appearing in gas phase fragmentation of furoxans.

Similar to the case of **PFT**, the surface-sensitive N 1s core level spectra of **BPFT** on the gold surface were obtained before and after irradiation and are shown in Figure 2(c, d). The binding energies of the N1 and N2 components of **BPFT** are 405.2 and 401.2 eV, respectively. Although the N1 component was smaller than the N2 component, their intensity ratio was closer to 1:1 than that of **PFT**. This means that the $-\text{O}-\text{N}^+-\text{O}$ group of **BPFT** combines with the Au surface relatively more stably compared to **PFT**, thus resulting in less ring-opening or deoxygenation of **BPFT** during adsorption.

Upon EUV-irradiation of the **BPFT** film on the gold surface, the N2 peak increased (about 30%) whereas the N1 peak decreased, as shown in Figure 2(d). The increase of the N2 component after irradiation can be interpreted as a result of conversion of the N1 component into the N2 component by ring-opening or deoxygenation reactions of furoxans to form the corresponding dinitrosoalkene or furazan, as observed in the case of **PFT**. Although it is difficult from the experiments to estimate how much ring-opening and deoxygenation occurred on the surface, given that the oxygen did not decrease in the O 1s core level of **BPFT** after irradiation, ring-opening was considered to be more prevalent than deoxygenation for furazan formation. In addition, after irradiation, the N1 components did not completely disappear, with approximately 27% of the N1 component before irradiation remaining. The existence of many $-\text{O}-\text{N}^+-\text{O}$ groups (N1 components) of **BPFT** on the surface even after irradiation indicates that **BPFT** is more stable than **PFT** and therefore responds less sensitively to EUV.

In summary, the furoxans **PFT** and **BPFT** were deposited on a gold surface and their conversion reactions were initiated by EUV. In the case of **PFT**, ring-opening and deoxygenation occurred together at the beginning of adsorption, leading to diverse adsorption states. Upon irradiation of **PFT** with EUV, it is likely that NO was released not only from the $-\text{O}-\text{N}^+-\text{O}$ group but also from the dinitrosoalkene generated by ring opening. In the case of **BPFT**, $-\text{O}-\text{N}^+-\text{O}$ groups were maintained to be more stable compared to the case of **PFT** during adsorption and ring-opening then takes place mainly, rather than NO release upon EUV irradiation. These results suggest that the structural modification of furoxan could affect the adsorption and EUV-induced reactions on gold surface.

Experimental

Au surfaces were cleaned so as to be free of C contaminants by Ar ion sputtering in an ultra high vacuum chamber (preparation chamber) maintained at 2.0×10^{-10} torr. After confirming the absence of contaminants using PES, the gold surfaces were moved in situ to a chemical reaction chamber ($\sim 10^{-6}$ torr) to deposit **PFT** and **BPFT** molecules by thermal evaporation. After depositing the molecules for 5-20 min,

the samples were moved back to the analysis chamber (1.0×10^{-10} torr) to check if the molecules had been absorbed on the surfaces through C 1s, N 1s, S 2p, and O 1s core level spectra.¹² The HRPES spectra were taken using a commercial electron analyzer (PHOIBOS 150, SPECS) at normal emission. The binding energies of the Au 4f core levels and the Fermi level of the bulk Au were used for calibrating the binding energy.

Acknowledgments. This research was supported by Basic Science Research Program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (Grant No. 2009-0074468). C. C. Hwang acknowledges financial support by the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (MEST) (Grant No. 2009-0083380 & 2011-0009427). The experiments at PLS were supported in part by MEST and POSTECH.

References

1. (a) Murcia, M. J.; Naumann, C. A. *Biofunctionalization of Fluorescent Nanoparticles in Biofunctionalization of Nanomaterials*; Kumar, C. WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2005; Chap 1, p 1.
2. (a) Jung, Y. J.; La, Y.-H.; Kim, H. J.; Kang, T.-H.; Ihm, K.; Kim, K. J.; Kim, B.; Park, J. W. *Langmuir* **2003**, *19*, 4512. (b) La, Y. H.; Kim, H. J.; Maeng, I. S.; Jung, Y. J.; Park, J. W. *Langmuir* **2002**, *18*, 301.
3. Heister, K.; Zharnikov, M.; Grunze, M.; Johansson, L. S. O.; Ulman, A. *Langmuir* **2001**, *17*, 8.
4. Fresco, Z. M.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2005**, *127*, 8302.
5. Sugimura, H.; Sano, H.; Lee, K.-H.; Murase, K. *Jpn. J. Appl. Phys.* **2006**, *45*, 5456.
6. Turchanin, A.; El-Desawy, M.; Götzhäuser, A. *Appl. Phys. Lett.* **2007**, *90*, 053102.
7. (a) Nandivada, H.; Chen, H.-Y.; Bondarenko, L.; Lehann, J. *Angew. Chem. Int. Ed.* **2006**, *45*, 3360. (b) Sun, X. L.; Starbler, C. L.; Cazalis, C. S.; Chaikof, E. L. *Bioconjugate Chem.* **2006**, *17*, 52. (c) Lee, J. K.; Chi, Y. S.; Choi, I. S. *Langmuir* **2004**, *20*, 3844.
8. Hwang, H. N.; Heo, J. M.; Kim, J. S.; Park, J. W.; Hwang, K.-J.; Hwang, C.-C. *J. Phy. Chem. C* **2009**, *113*, 16027.
9. Kim, C. O.; Jung, J. W.; Kim, M.; Kang, T. H.; Ihm, K.; Kim, K. J.; Kim, B.; Park, J. W.; Nam, H. Y.; Hwang, K.-J. *Langmuir* **2003**, *19*, 4504.
10. (a) Hwang, K.-J.; Kim, S. K.; Shim, S. C. *Chem. Lett.* **1998**, *8*, 859. (b) Hwang, K.-J.; Jo, I.; Shin, Y. A.; Yoo, S.; Lee, J. H. *Tetrahedron Lett.* **1995**, *36*, 3337.
11. Koo, H. S.; Park, K. M.; Hwang, K.-J. *Bull. Korean Chem. Soc.* **2010**, *31*, 3583.
12. Hwang, H.-N.; Kim, H.-S.; Kim, B.; Hwang, C. C.; Moon, S. W.; Chung, S. M.; Jeon, C.; Park, C. Y.; Chae, K. H.; Choi, W. K. *Nucl. Instrum. Methods Phys. Res. A* **2007**, *581*, 850.
13. (a) Xu, B.; Liu, X.; Haubrich, J.; Friend, C. M. *Angew. Chem. Int. Ed.* **2009**, *48*, 4206. (b) Xu, B.; Liu, X.; Haubrich, J.; Friend, C. M. *Nat. Chem.* **2010**, *2*, 61.
14. Curran, D. P.; Fenk, C. J. *J. Am. Chem. Soc.* **1985**, *107*, 6023.
15. Paton, R. M. *Comprehensive Heterocyclic Chemistry II*, Storr, R. C. Pergamon: United Kingdom, 1996; Chap. 4.
16. Georgy, M.; Boucard, V.; Debleds, O.; Zotto, C. D.; Campagne, J.-M. *Tetrahedron* **2009**, *65*, 1758.
17. (a) Ovchinnikov, I. V.; Epishina, M. A.; Molotov, S. I.; Strlenko, Y. A.; Lyssenko, K. A.; Markhova, N. N. *Mendeleev Commun.* **2003**, *13*, 272. (b) Medana, C.; Gasco, A. *J. Mass. Spectrom.* **1998**, *33*, 1037.