Two-dimensionally Chiral Monolayer of Atropisomeric Compounds on Gold

Masayoshi Murakami, Tsukasa Torimoto, and Bunsho Ohtani
Graduate School of Environmental Earth Science and Catalysis Research Center, Hokkaido University
Sapporo 001-0021, Japan

We have reported a self-assembled monolayer (SAM) of an atropisomeric compound with two thiol groups, 1,1'-binaphtalene-2,2'-dithiol (BNSH) [1]. When a gold substrate is dipped in an ethanolic solution of BNSH, SAM is formed on the surface of gold. In direct scanning tunneling microscopy (STM) observation of the structure of SAM, a well-ordered two-dimensional arrangement was detected. The arrangements in (*R*) and (*S*)-BNSH SAMs are of mirror images with respect to each other. This SAM of BNSH was found to be applicable to 'all-or-none' chiral discrimination of phenyalanine or thalidomide [2, 3]. Here we study the influence of gold substrates and conditions for the SAM formation on the structure of the two-dimensional arrangement.

A gold (111) facet of a single crystal and a gold film were used as the substrate to be modified with (*R*) or (*S*)-BNSH. The gold (111) facet of a single crystal was prepared by Clavilier's method. The gold film was prepared by vapor deposition on mica sheets. To confirm (111)-orientation of the gold substrates and to examine the behavior of the BNSH attached on gold was used cyclic voltammetry. These gold substrates were flame-annealed in city gas/oxygen flame just before the modification. BNSH SAM on gold substrates was prepared by rinsing the gold substrate with dilute ethanolic solutions (0.005 mmol dm^{-3}, containing 10 mmol dm^{-3} potassium hydride) of (*R*) or (*S*)-BNSH. After modification the substrates were rinsed thoroughly with ethanol.

Figure 1 shows cyclic voltammograms of the gold substrates in 0.1 mol dm^{-3} sulfuric acid. Since an oxidation peak at 1350 mV vs. Ag|AgCl and a reduction peak at 900 mV vs. Ag|AgCl appeared sharply, the surface of gold substrates are of (111)-orientation. The roughness factors, which were determined from the reduction peak, were ca. 1.46 and 1.2 for the gold film and the gold (111) facet, respectively. In the STM observations of gold substrates, they had wide terraces with some hundreds nm^2.

In the STM images, Figure 2, of the gold film modified with (*R*) or (*S*)-BNSH, two parts, an ordered part and a not ordered part, were seen. The height of the former was relatively lower than the latter. Higher resolution image of the ordered part depicts that the ordered structure consisted of combination of balls (white, the size of which roughly corresponds to a naphthalene moiety in BNSH) and holes (dark). Three triangles composed of six balls surround a hole, and different rotating directions could be seen. Such structure is seen in all ordered parts; the two-dimensional structure is chiral in molecular arrangements due to the chirality of BNSH. According to the previous report [1], rotating directions are counter-clockwise and clockwise for (*R*) and (*S*)-BNSH, respectively. These were also the case for the gold films used in this study.

In Figure 2(a), the ordered part 'domain' was separated into three parts, left-center-right. A fence-like structure was seen at the boundary of domains. Although in all domains a direction of the arrangement was commensurate with a gold substrate, on both sides of the fence, a misalignment of arrangement was observed. This suggests that during SAM formation many seeds of SAM are created at various points on the gold substrate at same time and the domains are formed from them. When the domains with misalignment collide, the fence-like boundary structure is produced.

REFERENCES

1. B. Ohtani, A. Shintani, K. Uosaki, J. Am. Chem. Soc., 121, 6515 (1999).
2. T. Nakanishi, N. Yamakawa, T. Asahi, T. Osaka, B. Ohtani, K. Uosaki, J. Am. Chem. Soc., 124, 740 (2002).
3. T. Nakanishi, N. Yamakawa, T. Asahi, N. Shibata, B. Ohtani, T. Osaka, Chirality, in press (2004).

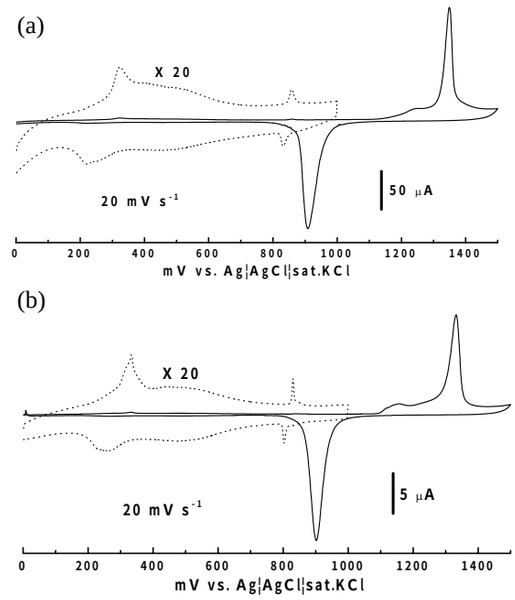

Figure 1. Cyclic voltammograms of (a) the gold film and (b) the gold (111) facet in 0.1 mol dm^{-3} H_2SO_4.

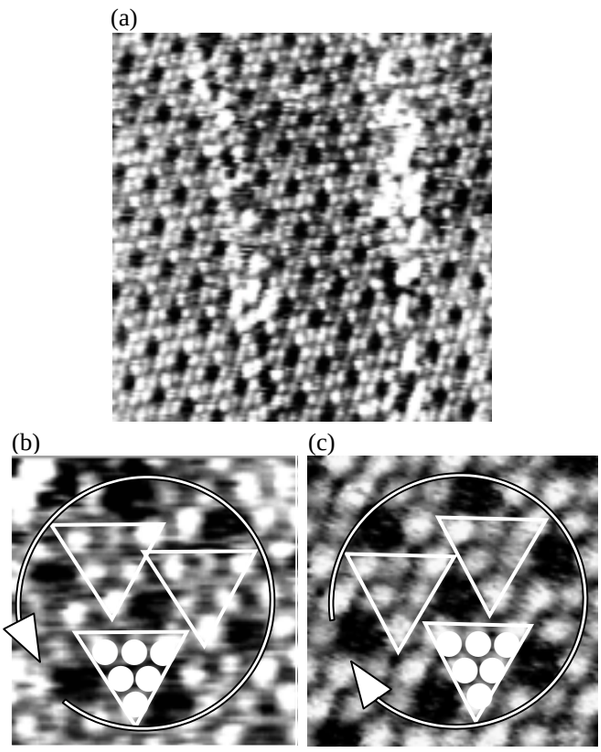

Figure 2. Typical STM images of parts of gold films modified with (*R*)-BNSH (a) 25 × 25 nm, (b) 6 × 6 nm and with (*S*)-BNSH (c) 6 × 6 nm. Bias voltages were (a), (b) 650 and (c) 100 mV. Tunneling currents were (a) 474, (b) 500, and (c) 60 pA.