Development of New Methods for Single-Molecule Measurements under Electrochemical Environment

Yuzu Kobayashi[1,2], Raymond Wong[1], Misun Hong[1], Yasuyuki Yokota[1], Jun Takeya[2] and Yousoo Kim[1,3]

[1] *Surface and Interface Science Laboratory, RIKEN, Wako, Saitama 351-0198, Japan*
[2] *Department of Advanced Materials Science, The Univ. of Tokyo, Kashiwa, Chiba 277-8561, Japan*
[3] *Department of Advanced Chemistry, The Univ. of Tokyo, Bunkyo-ku, Tokyo 113-88656, Japan*

yuzu.kobayashi@riken.jp

Tracking various chemical reactions including electrochemical reactions at the single-molecule level is expected to yield a great deal of knowledge from both fundamental and applied aspects. EC-STM, a combination of scanning tunneling microscopy (STM) and electrochemical (EC) measurements, allows direct observation of electrochemical interfaces with high spatial resolution [1]. In this study, we report on a methodology to track redox reactions of single-molecules using EC-STM. This was made possible by the self-assembled monolayer (SAM) fabrication of structurally rigid tripodal molecules with a tethered ferrocene (Fc) moiety [2]. By preparing a mixed SAMs with the molecules with and without Fc moieties, we could stably deposit Fc species on Au (111) electrode in an isolated and dispersed state, which enables us to observe clear changes in the EC-STM images upon the redox reaction of the single Fc derivative [3].

A mixture of 8,13-trimercaptotriptycene (Trip) and its Fc derivative (Fc-Trip, Fig. 1a) was deposited on a Au(111) electrode (the molecules were provided by the Fukushima Lab., Chemical Biology Laboratory, Tokyo Institute of Technology, and the Suzuki Lab., Graduate School of Science, Hokkaido University). Cyclic voltammetry (CV) was performed with a potentiostat (HZ-7000, Hokuto Denko) at a sweep rate of 0.1 V/s in 0.1 M $HClO_4$ solution. STM measurements were performed using an MS-10 STM (Bruker), controlled by a NanoScope V (Bruker). A Pt/Ir wire coated with Apiezon wax was used as a tip in a home-made electrochemical cell. The sample potential (E_{sample}) was varied from 0.2 V (vs Ag/AgCl) to 0.4 V while the potential difference between the tip and the sample was kept at 0.3 V.

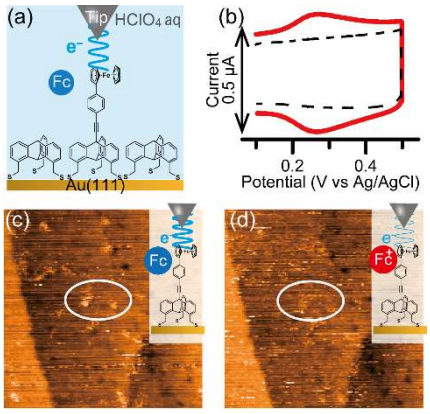

Fig. 1. (a) Schematics of the sample. (b) CV of Trip and Fc-Trip mixed SAM. (c)(d) EC-STM images (90×90 nm^2) taken at (c) 0.2 and (d) 0.4 V.

The CV results are shown in Fig. 1b, where the peak originating from the redox reactions of Fc-Trip is observed (dotted line is only for Trip), indicating that the redox potential of Fc-Trip is ~0.3 V. Corresponding EC-STM images are shown in Fig. 1c, d. While the bright spots derived from Fc-Trip are observed at E_{sample} = 0.2 V (the tip potential E_{tip} is 0.5 V), as indicated by white circles, the bright spots almost disappeared at E_{sample} = 0.4V (E_{tip} = 0.7 V). We confirmed that the change of the height is reversible with respect to the applied potentials. The height of the bright spot in the EC-STM images reflects the electron transfer rate through the redox molecule between the tip and the sample.

The novel strategy using a tripodal molecules has made it possible to measure isolated small molecules (a few Å) using EC-STM. In the presentation, we will also discuss the new method for the tip fabrication, which can pave the way for advanced measurements such as tip enhanced Raman spectroscopy [4] and accelerate progress in the field of surface electrochemistry.

[1] Y. Yokota *et al., J. Phys. Chem. C*, **111**, 7561 (2007). [2] F. Ishiwari *et al., J. Am. Chem. Soc.*, **141**, 5995 (2019).
[3] Y. Kobayashi *et al., J. Phys. Chem. C*, **127**, 746 (2023). [4] Y. Yokota *et al., J. Phys. Chem. C.* **123**, 2953 (2019).