Supplementary Material (ESI) for Chemical Communications

Supporting Information for "TNT Adsorption on Au (111): Electrochemistry and Adlayer Structure"

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Experimental Section

TNT (1g/L in acetonitrile, Sigma-Aldrich), 4-NT (Acros Organics) and 2,4-DNT (TCI) were used as received. Electrolyte solution was prepared with ultrapure $HClO_4$ (Aldrich Chemical Co., 99.999%) and Milli-Q water (Milli-Q, ≥ 18.2 MΩ, TOC < 4 ppb). Molecular models of TNT adlayer were built in HyperChem 6.0 and Materials Studio 3.0.

The preparation for the Au(111) crystal and electrolyte solution was the same procedure as reported in the literature.[1] Briefly, a well-defined Au(111) facet using for the STM experiments was prepared by crystallization of molten ball formed at the end of a Au wire (99.999%) in a hydrogen-oxygen flame.[2,3] For electrochemical detections, a good single-crystal Au(111) disk of ca. 8 mm in diameter and ca. 5 mm in height was used. Before each measurement, the Au (111) electrode was further annealed in a H_2-O_2 flame and quenched in Mill-Q water saturated with H_2.

Electrochemical measurements including cyclic voltammetry and stripping experiments were performed by the hanging meniscus method in a three-compartment electrochemical cell with using an EG&G Princeton Applied Research (PAR) advanced electrochemical system (PARSTAT 2263) controlled by a microcomputer with EG&G PARC M250 software as reported previously.[4] A reversible hydrogen electrode (RHE) and a platinum wire were used as reference and counter electrodes, respectively. The solutions were deaerated with high purity N_2 before experiments. All electrode potentials were reported with respect to the RHE in 0.1 M $HClO_4$. All experiments were performed at room temperature (about 298 K).

Electrochemical STM experiments were carried out by using a NanoScope E microscope (Digital Instrument Inc., Santa Barbara, CA) in 0.1 M $HClO_4$. The tunneling tips were prepared by electrochemical etching of a tungsten wire (0.25 mm in diameter) in 0.6 M KOH. To minimize faradic current, the sidewalls of the tips were sealed with transparent nail polish. All the STM images were collected in the constant-current mode.

Reference:

1. J. Clavilier, D. Armand, S.G. Sun, M. Petit, *J.Electroanal.Chem.* 1986, **205**, 267.
2. J. Clavilier, R. Faure, G. Guinet, R. Durand, *J. Electroanal. Chem.* 1979, **107**, 205.
3. A. Hamelin, L. Stoicoviciu, S.-C. Chang, M.J. Weaver, *J. Electroanal. Chem.*1991, **307**, 183.
4. H.X. Zhang, A.M. Cao, J.S. Hu, L.J. Wan, S.T. Lee, *Anal. Chem.* 2006, **78**, 1967.

Computational Details

Theoretical calculations on periodic structures were carried out with DMol 3 in Materials Studio 3.1 (Accelrys, San Diego, CA).

To determine the exact orientation of TNT on Au(111), DFT calculations have been carried out. The periodic structure and the sites of three nitro groups were extracted from the STM images. Then, we change methyl group's site of two TNT molecules in one unit cell, respectively. Thus, nine possible models can be proposed and shown as follows (a-i). Note that only eight TNT molecules are shown in the models. The whole system energies of nine models were computed by DFT calculations performed using the PW91 generalized gradient approximation (GGA). The results indicate that model (a) has lowest energy (-20295.694 KJ/mol). This is in agreement with the STM result. Namely, the brighter spot in STM image of an individual TNT molecule corresponds to the methyl's para nitro group.