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TNT adsorption on Au(111): electrochemistry and adlayer structure†

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Electrochemistry and adlayer structure of trinitrotoluene (TNT) on an Au(111) electrode were investigated using cyclic voltammetry and *in situ* electrochemical scanning tunneling microscopy (ECSTM).

Trinitrotoluene and its derivatives are typical explosive compounds. Owing to their importance in environmental protection and anti-terrorism, the study of these compounds has attracted considerable attention from chemists,[1–3] and special devices and sensors have been developed to detect and analyze TNT and its derivatives.[4,5] Among various methods, electrochemical techniques have been proved useful for detecting and characterizing these compounds due to their high sensitivity and simplicity, and ease for fabricating inexpensive and portable detectors.[6] So far, various active and efficient working electrodes have been found or fabricated including functionalized carbon nanotubes, mesoporous silica, polycyclic aromatic hydrocarbon-modified electrodes and various metals for the electrochemical measurement of TNT and its derivatives.[7–14]

In developing a new detection technique, understanding molecular adsorption on the electrode surface is a challenging issue in the study of TNT. The adsorption and desorption, and the adlayer structure of TNT on electrode surfaces is of importance in tracing concealed explosives and a prerequisite in sensor design.[15,16] However, the electrochemistry and adlayer structure of explosive compounds on electrode surfaces, in particular on single crystal electrode surfaces, is rarely reported, although the recent advent of STM and related probe microscopy has allowed us to investigate the adsorption of these surfaces at the atomic/molecular level in solution.[17–19]

Herein, we report, for the first time, an *in situ* electrochemical STM study on the adsorption of TNT on single crystal Au(111) surfaces in aqueous solution. The adlayer structure and structural transition of TNT molecules have been investigated by high resolution STM imaging. It is found that TNT molecules adsorb on the Au(111) surface in a flat-lying orientation and form a well-ordered adlayer with a $(2\sqrt{3} \times 4\sqrt{3})$ symmetry. Moreover, higher electrochemical sensitivity of TNT (down to ppb levels) on Au(111) has been revealed. Since high quality gold films with (111) surfaces can be easily prepared, the present results are significant for applications for TNT detection.

Fig. 1A shows typical cyclic voltammograms (CVs) of Au(111) in 0.1 M $HClO_4$ solution without (line a) and with 600 ppb TNT (line b). It can be seen that the CV for bare Au(111) (line a) is consistent with the literature,[20] indicating that a well-defined surface is exposed to solution. The addition of TNT has induced new cathodic peaks (line b), which occur from *ca.* 410 mV. It is interesting that three well-defined TNT peaks at 370, 310, and 270 mV, respectively, can be clearly resolved in the stripping voltammogram (see the inset) with low scanning rate. As described in the literature,[21–24] the three irreversible peaks are correlated with the sequential reduction of the three nitro groups of TNT to hydroxylamine groups, which are finally converted into amine groups. In contrast, only one or two reduction peaks were observed in the detection of TNT with a polycrystalline gold electrode.[11–14] Fig. 1B shows two typical stripping voltammograms of Au(111) at low concentration of TNT. Note that a small reduction peak at 370 mV is still visible when the concentration is close to 0.4 ppb. This result indicates a high sensitivity of single crystal Au(111) electrodes to TNT. It can thus be concluded that the single crystal Au(111) electrode holds promising and important applications for electrochemical detection of ultra-trace TNT.

The electrochemical activity of the Au(111) electrode has also been estimated in 0.1 M $HClO_4$ containing either 4-nitrotoluene (4-NT) or 2,4-dinitrotoluene (2,4-DNT). It is found that 4-NT has only one reduction peak at 230 mV, while 2,4-DNT has two peaks at 320 and 270 mV, respectively (Fig. 2). It is indicated that the number of reduction peaks for Au(111) is dependent on the number of nitro groups on the

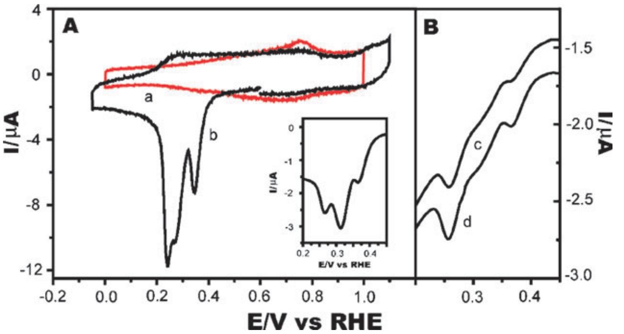

Fig. 1 (A) CVs for Au(111) in 0.1 M $HClO_4$ (line a) and 0.1 M $HClO_4$ + 600 ppb TNT (line b). The scan rate was 50 mV s^{-1}. The inset shows a typical stripping voltammogram recorded at 10 mV s^{-1}. (B) Stripping voltammograms for Au(111) in 0.1 M $HClO_4$ containing 0.4 (line c) and 1.0 ppb TNT (line d). The scan rate was 50 mV s^{-1}.

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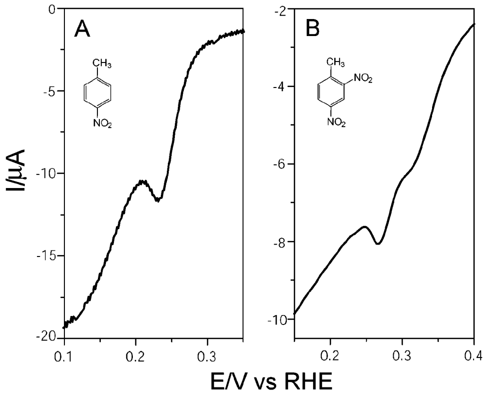

Fig. 2 Stripping voltammograms of Au(111) in 0.1 M $HClO_4$ solution containing (A) 6 ppm 4-NT and (B) 0.4 ppm 2,4-DNT.

aromatic ring, which is not the case for polycrystalline gold electrodes.[11–14] Therefore, the single crystal Au(111) may have potential in the electrochemical detection of nitroaromatic compounds with distinguishable voltammogram features.

The adlayer structure of TNT on Au(111) is investigated by *in situ* electrochemical STM. Fig. 3A shows a typical large-scale STM image of TNT on Au(111) acquired under potential control of 550 mV. It is evident that the atomically flat terrace is covered by an ordered adlayer of TNT. The molecular rows are parallel to the ⟨121⟩ direction of underlying Au(111). The details of the internal molecular structure, orientation, and packing arrangement are revealed by a higher resolution STM image in Fig. 3B. Each TNT molecule in the image can now be characterized as a set of three spots. Note that one of spots is usually brighter than the other two. The overall shape of the STM contrast of an individual TNT is qualitatively comparable to the electronic density of the lowest unoccupied molecular orbital (LUMO) shown in Fig. 3C. The brighter spot (red circle) is therefore ascribed to the methyl's *para* nitro group, while the other two are the *ortho* nitro groups (yellow circles).

Careful inspection reveals that the orientation of TNT along arrows I and II (Fig. 3B) is not identical but depends on its position. The TNT molecules along arrow I are always rotated by 60 or 120 ± 2° with respect to those along arrow II. In addition, the TNT molecules along the arrows I and II appear with the same feature, although the molecular orientation is different. This also indicates a strong influence of the TNT–Au(111) interaction on the formation of the ordered adlayer. The intermolecular distances *a* and *b* are measured to be 1.1 ± 0.05 nm and 1.95 ± 0.05 nm, respectively. The crossing angle α is 60 ± 2°. Therefore, a unit cell with $(2\sqrt{3} \times 4\sqrt{3})$ symmetry can be concluded. Each unit cell is composed of two TNT molecules. Based on the above analysis, a schematic model for the TNT adlayer is tentatively proposed in Fig. 3D. All the TNT molecules are assumed to flatly adsorb on the threefold hollow sites of underlying Au(111). Note that other possible orientations of TNT have been taken into account in the present study. However, only the proposed model has minimum steric repulsion between neighboring TNT molecules. Further DFT calculation has confirmed that the as-proposed model in Fig. 3D is an energetically stable system (see ESI†).

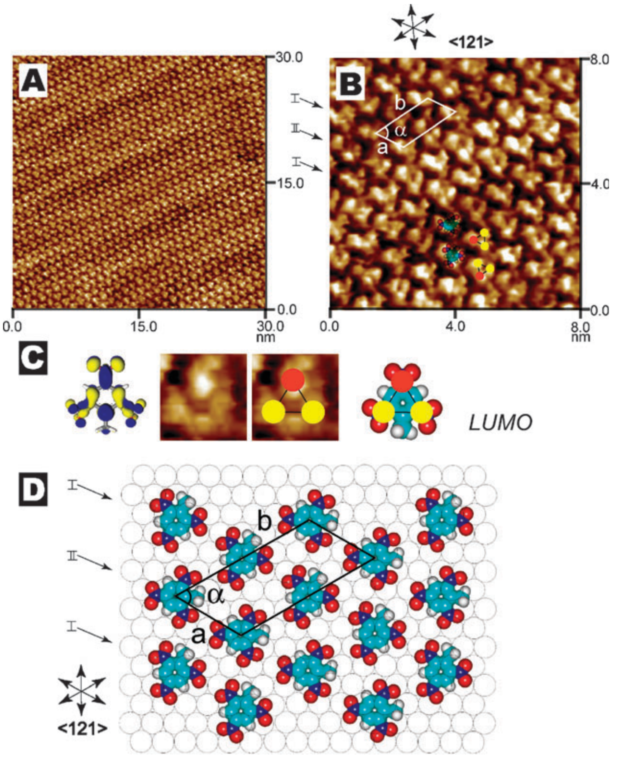

Fig. 3 (A) Large-scale and (B) high-resolution STM images of TNT adlayer on Au(111). E = 550 mV, $E_{\mathrm{bias}} = -164$ mV, I_{tip} = 1.23 nA. (C) Close-up STM image of an individual TNT molecule and the LUMO state of TNT (left). (D) Proposed structural model for the ordered adlayer.

The ordered structure has been consistently observed at potentials positive from 550 mV. With negative shifting of the electrode potential, the reduction of nitro groups sets in. Fig. 4A–C show typical STM images acquired at 400, 340, and 240 mV (marked by arrows A, B and C in the stripping voltammogram). It is interesting that only the $(2\sqrt{3} \times 4\sqrt{3})$ structure is observed in the three STM images. In addition, almost the same appearance can be seen for individual TNT molecules, although the reduction of nitro groups to hydroxylamine or amine groups may occur in this potential region. This is possibly due to the strong N–Au(111) interaction and the stability of phenyl rings on substrate surfaces in the reduction process, resulting in a stable adlayer on Au(111). When the electrode potential is reduced to *ca.* 50 mV, the desorption of molecules is observed.

In summary, Au(111) is found to be a sensitive electrode for the explosive compound TNT. A featured CV with three well-defined cathodic peaks is recorded on Au(111) in $HClO_4$ solution containing TNT. *In situ* electrochemical STM observation reveals that TNT molecules can form a well-ordered adlayer with a $(2\sqrt{3} \times 4\sqrt{3})$ structure and adsorb on Au(111) in a flat-lying orientation. In addition, the structures at different reduction potentials are also investigated. The results reported here are important in understanding the adsorption of TNT on metal surfaces and detecting explosive compounds by electrochemical method.

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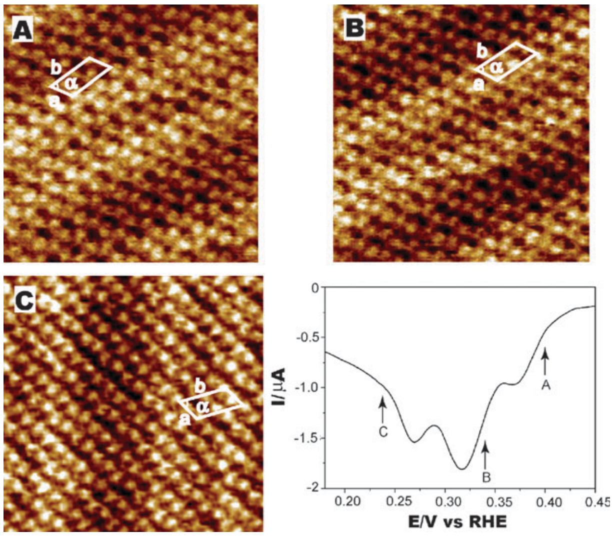

Fig. 4 Sequence of typical STM images (10 × 10 nm^2) during the reduction of TNT on Au(111) in 0.1 M $HClO_4$. (A) E = 400 mV, E_{bias} = −169 mV, I_{tip} = 0.99 nA. (B) E = 340 mV, E_{bias} = −184 mV, I_{tip} = 1.12 nA. (C) E = 240 mV, E_{bias} = −107 mV, I_{tip} = 1.3 nA. The corresponding potentials are shown in the stripping voltammogram for Au(111) in $HClO_4$ + TNT.

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