Communication

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Direct Visualization of an Aniline Admolecule and Its Electropolymerization on Au(111) with in Situ Scanning Tunneling Microscope

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Atomic force microscopy, scanning tunneling microscopy, and spectroscopy (STM/STS) have been used to probe polyaniline (PAN) films, revealing metallic and insulating granules formed in the salt- and base-form of emeraldine.[1−4] However, the size and the structure of PAN molecules within a conducting granule are usually unknown, which makes it difficult to tie PAN's conductivity with molecular specificity. Meanwhile, the advances of scanning probes has enabled control of local polymerization of diacetyene molecules, and has yielded the conformations of polythiophene molecules adsorbed on graphite surface.[5−7] Recently, in situ STM was used to visualize polythiophene molecules produced by pulsing the potential of an iodine-coated Au(111) electrode in dichloromethane.[8,9] Here, we illustrate the use of molecular resolution STM to examine the structure of an aniline adlayer and the subsequent oxidative polymerization on a Au(111) single-crystal electrode in sulfuric acid.

Figure 1a shows the cyclic voltammogram recorded at 50 mV/s with a Au(111) electrode in 0.1 M sulfuric acid containing 30 mM aniline. The Au(111) electrode was a single crystal bead made by melting the end of a gold wire ($\phi = 1$ mm).[10] This CV profile was stable against potential cycling between 0.05 and 0.9 V (vs reversible hydrogen electrode, RHE), as oxidative polymerization of aniline would not occur until $E > 1$ V. Two pairs of peak, denoted A1/C1 and A2/C2, appeared at 0.47 and 0.62 V, which are ascribable to the adsorption/desorption of aniline molecules and the subsequent structure changes. This CV profile is reminiscent of those of pyridine, 2,2′-bipyridine, and 4,4′-bipyridine, on a Au(111) electrode.[11−13]

The experimental setup of in situ STM is already described.[14] Figure 1b shows a constant-current STM image obtained with a Au(111) electrode at 0.8 V in 0.1 M sulfuric acid plus 30 mM aniline. In this image long-range ordered adlattices were readily discerned amid randomly distributed islands. The ordered arrays are due to adsorbed aniline monomers, and the protruded islands, raised by 0.25 nm above the terrace, were aggregated gold adatoms injected from the Au(111) surface upon the lift of reconstruction.[14] It was possible to prepare the unreconstructed Au(111)−(1 × 1) surface free of protruded islands by using the proper annealing and quenching process. In situ STM shows that a smooth, unreconstructed Au(111) surface could result in a highly ordered aniline adlayer and extended linear PAN molecules at $E > 1$ V.

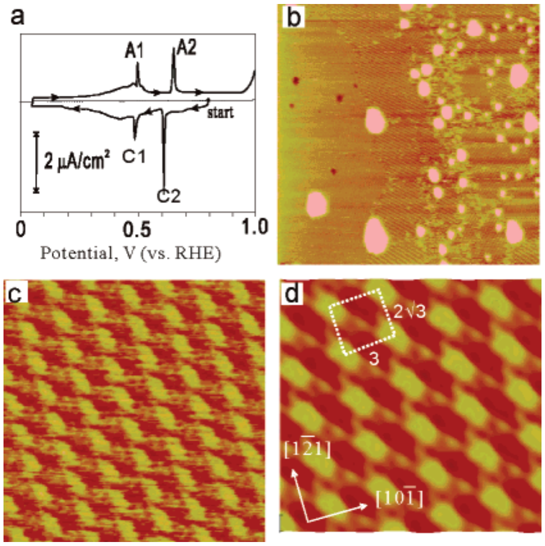

Figure 1. Cyclic voltammogram recorded at 50 mV/s with Au(111) in 0.1 M H_2SO_4 + 30 mM aniline (a). Constant-current STM scans ((b) 50 × 50 nm, (c) 7 × 7 nm, (d) 5 × 5 nm) acquired at 0.9 V with a bias voltage of −300 mV and a feedback current of 5 nA. The image in panel d was treated with a Fourier transform method.

Shown in Figure 1c is a higher resolution STM scan, which yielded the internal arrangement of aniline admolecules. After being filtered with a Fourier transform technique, this image is further highlighted in Figure 1d. This ordered array has a rectangular unit cell with two edges aligned in the $\langle 101 \rangle$ and $\langle 121 \rangle$ directions and measured 0.9 and 1.0 nm in length. Prior to the dosing of aniline, we obtained atomic resolution STM with the Au(111) single-crystal electrode to determine how aniline admolecules were arranged. The structure of aniline in Figure 1d would fit a symmetry of $(3 \times 2\sqrt{3})$rect. Aside from the prominent corner spots, a discernible weak spot is seen in the middle of the unit cell. Tentatively, the former could be aniline molecules adsorbed horizontally; whereas the latter was an edge-on aniline admolecule. This contention could be in line with the result of a previous study employing surface enhanced Raman spectroscopy.[16]

Shifting the potential from 0.9 to 1.05 V resulted in oxidative polymerization of aniline, yielding a series of STM images shown in Figure 2a−c. The first image in Figure 2a, acquired at 0.9 V, highlights a remarkably ordered array of aniline on the Au(111)−(1 × 1) surface. The inset in Figure 2a shows a high-resolution scan, which indicates the $(3 \times 2\sqrt{3})$rect−aniline structure described earlier. There was hardly any defect in a 50 × 50 nm scan area, and the extent of ordering apparently exceeded the scan area. The atomically flat Au(111)−(1 × 1) surface made the formation of this highly ordered aniline adlayer possible. Figure 2b,c were STM images collected 1 and 20 min after the switch of potential to 1.05 V. Momentary instability in the STM imaging was noted in Figure 2b, but it settled down shortly. The most distinct features of these STM images are the hitherto unseen line segments aligned preferentially in the $\langle 121 \rangle$ direction of the Au(111) surface. The number and the length of the newly formed line segments grew with time. Close inspection of this STM image disclosed that not all protruded stripes exhibited the same intensity. They were 0.1 or 0.4 nm higher than the dimmest rows ascribed to aniline admolecules. All the brighter stripes were PAN molecules, although the origin for their difference in corrugation is not clear. They could be different in thickness or in molecular structure. Note that

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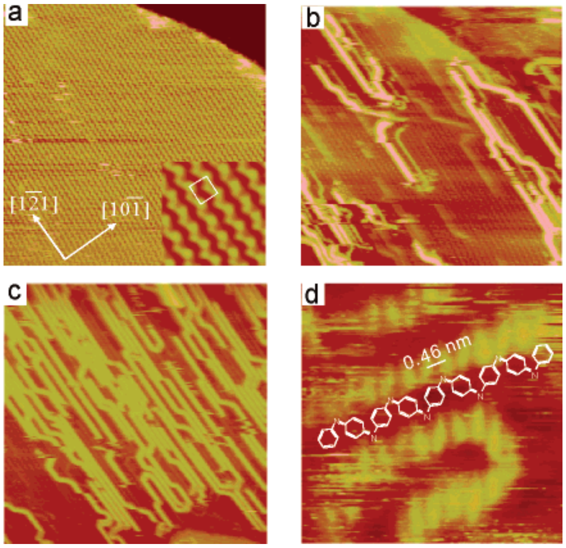

Figure 2. Time-dependent in situ STM images recorded with Au(111) at 0.9 V (a), and 1.05 V (b−c). The images in panels b and c were collected 1 and 20 min after the shift of potential from 0.9 to 1.05 V. Scan areas (a−c) are 50 × 50 nm and (d) 6 × 6 nm.

polymers with more extended molecular conjugation result in higher corrugation height than a monomer in an STM image, as observed previously for diacetylene and polythiophene.[6,8,9]

The distinct preferential alignment of PAN molecules in the ⟨121⟩ direction indicates that the process of polymerization is strongly anisotropic under the present condition. To our knowledge, direction-dependent polymerization, although noted previously for diacetylene,[6] has not been reported for aniline. Judged from the STM result in Figure 2c, roughly 100 aniline monomers were chained to produce a 50 nm long linear PAN molecule with a molecular weight of ca. 900 g/mol. It is remarkable to recognize that it took only a simple switch of potential to accomplish this. Bent and folded PAN chains were inevitable deformations. Most PAN molecules were imaged as parallel lines, suggesting no cross-link between neighboring PANs.

Shown in Figure 2d is a further high-resolution STM scan to reveal the internal molecular structure of PAN chains. This image was obtained in an experiment different from that of Figure 2a−c. It is now clear that a linear PAN molecule actually consisted of 10 oval-shaped protrusions arranged in a zigzagged fashion. Two neighboring ovals separated by 0.46 nm measured from their geometric centers. This corresponds well to the ideal spacing between two phenyl groups within PAN made by the head-to-tail coupling process.[17,18] The 1 nm spacing between two neighboring polyaniline chains is also consistent with the theoretical value expected for the zigzag arrangement of the phenyl groups in PAN. PAN chains were found to be the predominant features in STM imaging. We could not identify any feature ascribable to anionic dopant. Since the incorporation of dopant can alter substantially the conductivity of PAN,[2−4] we will do more STM imaging experiments in different electrolyte to address this issue.

In the present study stable STM imaging was possible only for PAN not thicker than three layers. Preliminary STM results obtained with multilayer polyaniline system indicate prominent linear conformation, as seen in Figure 2b,c. However, four layered PAN on Au(111) was not conductive enough to render stable STM imaging. To further correlate the linear conformation of PAN with the structure of the aniline monomer, we examined the aniline polymerization on a rougher Au(111) surface. The resultant STM images showed mostly curvy PAN chains, which indirectly supports our contention that electropolymerization of aniline was a surface-guided process at the initial stage.

In conclusion, we have used in situ STM imaging to reveal the structure of an aniline adlayer and the subsequent electropolymerization of aniline on Au(111). The degree of ordering in the aniline adlayer controls the extent of linearity of the PAN molecule. A switch of potential can produce linear PAN spanning 50 nm or more. Molecular resolution STM discerns the internal molecular structure of PAN. The measured spacing between two phenyl rings suggests that the as-formed PAN consists of aniline molecules linked in a head-to-tail manner. However, our present STM results could not resolve whether solution aniline molecules were involved in the formation of PAN at the initial stage. It is fair to state that our present STM study has provided unprecedented insights into the structure of PAN produced potentiostatically. We are doing more STM experiments to unravel the polymerization of the aniline monolayer, the stability of PAN molecule, and the conductivity of a single PAN.

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Supporting Information Available: STM results obtained with PAN on rough Au(111). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Planes, J.; Samson, Y.; Chequettine, Y. *Appl. Phys. Lett.* **1999**, *75*, 1395.
(2) Jeon, D.; Kim, J.; Gallagher, M. C.; Willis, R. F. *Science* **1992**, *256*, 1662.
(3) Yau, S. T.; Barisci, J. N.; Spinks, G. M. *Appl. Phys. Lett.* **1999**, *74*, 667.
(4) Wu, C. G.; Chang, S. S. *J. Phys. Chem. B* **2005**, *109*, 825.
(5) Brun, M.; Demadrille, R.; Rannou, P.; Pron, A.; Travers, J. P.; Grevin, B. *Adv. Mater.* **2004**, *16*, 2087.
(6) Okawa, Y.; Aono, M. *Nature* **2001**, *409*, 683.
(7) Mena-Osteritz, E.; Meyer, A.; Langeveld-Voss, B. M. W.; Janssen, A. J.; Meijer, E. W.; Bauerle, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 2680.
(8) Sakaguchi, H.; Masumura, H.; Gong, H. *Nature* **2004**, *3*, 551.
(9) Sakaguchi, H.; Masumura, H.; Gong Abouelwafa, A. M. *Science* **2005**, *310*, 1002.
(10) Hamelin, A. *J. Electroanal. Chem.* **1996**, *407*, 1.
(11) Li, N.; Zamlynny, V.; Lipkowski, J.; Henglein, F.; Pettinger, B. *J. Electroanal. Chem.* **2002**, *524*, 43.
(12) Noda, H.; Minoha, T.; Wan, L.-J.; Osawa, M. *J. Electroanal. Chem.* **2000**, *481*, 62.
(13) Cai, W.-B.; Wan, L.-J.; Noda, H.; Hibino, Y.; Ataka, K.; Osawa, M. *Langmuir* **1998**, *14*, 6992.
(14) Itaya, K. *Prog. Surf. Sci*. **1998**, *58*, 121.
(15) Shue, C. H.; Yau, S. L.; Itaya, K. *J. Phys. Chem. B* **2004**, *108*, 17433.
(16) Holze, R. *J. Electroanal. Chem.* **1988**, *250*, 143.
(17) Huang, W. S.; Humphrey, B. D.; MacDiarmid, A. G. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2385.
(18) (a) Choi, S. J.; Park, S. M. *J. Electrochem. Soc.* **2002**, *149*, E26. (b) Shim, Y. B.; Won, M. S.; Park, S. M. *J. Electrochem. Soc.* **1990**, *137*, 538. (c) Duic, L.; Mandic, Z.; Kovac, S. *Electrochim. Acta.* **1995**, *40*, 1681.

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