

In Situ STM and Ex Situ XPS and NEXAFS of Polyaniline Molecules Adsorbed on Au(111)

In situ scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and near edge X-ray absorption fine structure (NEXAFS) have been used to examine the conformation of a monolayer of polyaniline (PAN) molecules produced by anodization of Au(111) single-crystal electrode in 0.10 M H₂SO₄ containing 0.030 M aniline. The as-produced PAN molecules could assume linear and meandering shapes when the potential of Au(111) was lower and higher than 1.0 V (vs. reversible hydrogen electrode). XPS and NEXAFS results indicate that the linear PAN presumed the form of emeraldine salt, made of PAN chains and (bi) sulfate anions. The amino-bisulfate linkages in PAN molecules were the anchoring points, which matched well with the dimension of the Au(111) support, thus enabling PAN molecules to stretch out in linear shape. PAN molecules became noticeably meandering when the potential was lowered. We attribute the dramatic changes in molecular shape to reorganization of bisulfate adsorption configuration on Au(111).

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Polyaniline (PAN), a century old conducting polymer, continues to evolve as intriguing materials with versatile applications. Modern probing tools such as scanning probes has shed new insights into the physical and electronic structures of PAN. These local probes are able to reveal molecular levels details of PAN, which has been rather difficult or impossible to achieve.

Scanning tunneling microscopy (STM) is well known for its sub-nanometer resolution, which has been used to probe the organization of polymeric materials in vacuum and in electrochemistry. We have taken advantage of STM to see how aniline molecules were adsorbed on Au(111) and their polymerization under anodization. On Au(111) aniline molecules are found to adsorb in highly ordered arrays and polymerize into polyaniline with well-defined linear shape spanning for 500 Å or more along some specific directions. These characteristics of PAN are thought to stem from a special lateral arrangement of aniline monomers and the co-adsorbed bisulfate anions. PAN molecules produced on rough gold electrode had poorly-defined shape.

In addition, X-ray photoelectron spectroscopy (XPS) and near edge X-ray fine structure spectroscopies are used to identify the chemical nature of PAN formed under conditions the same as those of STM. PAN molecules formed on Au(111) at potential at $E > 1.0$ V (vs. reversible hydrogen electrode) was predominantly the emeraldine salt, although molecular shapes changed so drastically as potential was lowered.

Linear polyaniline formed at 1.0 V on Au(111). We focus on the conformation of PAN molecule as a function of the electrochemical potential. The potential was intentionally set at $E = 1.0$ V where the rate of oxidation and polymerization of aniline was so slow that in situ STM was able to follow the transformation of aniline monomers arranging in $(3 \times 2\sqrt{3})$ rect to linear PAN molecules, bulging by 3.5 Å (Fig. 1a). Some aniline admolecules were oxidized to radical cations first, followed by reacting quickly with their neighbours to produce PAN molecules.

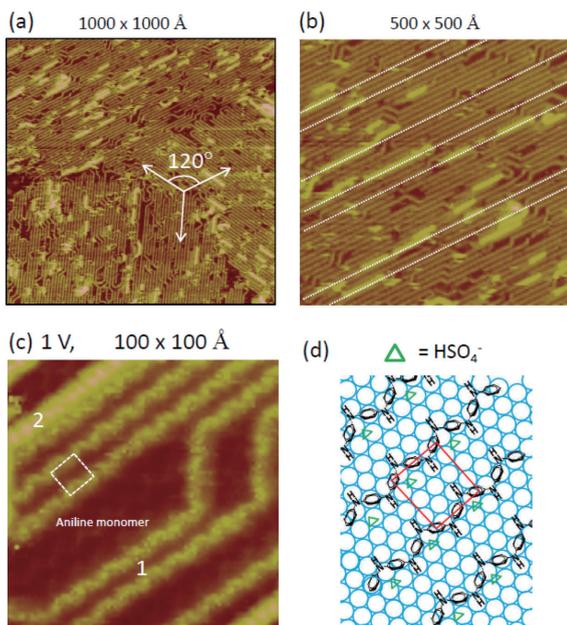


Fig. 1: In situ STM images obtained with Au(111) at 1.0 V in 0.1 M H_2SO_4 containing 0.03 M aniline. Three rotational domains of PAN molecules are seen in (a), followed by a higher resolution scan showing the formation of multilayer PAN. The molecular resolution scan in (c) discloses the internal molecular structure. A corresponding real-space model is shown in (d) with green triangles representing bisulfate anions bridging PAN molecules and the Au(111) substrate.

Depending on the length of time by holding potential at 1.0 V, PAN film with a thickness of sub-to multilayer could be formed. The intensity of PAN molecules in the STM image reflected the heights of PAN on Au(111). High-quality STM could be achieved on a 4-layer thick PAN as long as the feedback current was set lower than 1 nA. The as-formed PAN chains grew easily to 300 Å in length, and could reach 1000 Å. It all depended on the quality of the Au(111) surface. The key to prepare long and straight PAN molecules lies in making a well-ordered $(3 \times 2\sqrt{3})$ rect - aniline structure at 0.90 V prior to polymerization. These STM results indicate that anodization was effective in producing linear PAN molecular wires, although defects of 120° - bent or hairpin - like fold were always present.

The as-produced PAN admolecules were always aligned in three specific directions, the $\langle 110 \rangle$ directions of Au(111). Two neighbouring PAN chains were uniformly spaced by 10.4 Å, which equals to the length of the $2\sqrt{3}$ unit vector of the $(3 \times 2\sqrt{3})$ rect - aniline structure. This intermolecular

spacing persisted as PAN film grew thicker. The dotted lines marked in Fig. 1b are intended to show that PAN chains in the upper tiers perched on, not in between, the chains on the lower planes. This arrangement may be classified as molecular epitaxy, which is likened as layers of bricks used in constructing buildings. PAN chains lying in the lower planes acted as the template, which guided the subsequent growth of PAN.

Molecular-resolution STM imaging discerned the internal molecular structures of PAN molecules, as shown in Fig. 1c. Each PAN molecule was imaged as a chain of oval protrusions linked back-to-back in the main axis of the Au(111) substrate. All oval protrusions are attributed to the aromatic rings in a PAN molecule; two neighbouring rings separated by 4.5 Å from each other. Two nearest PAN chains were 10.4 Å apart, which corresponds to the length of a $2\sqrt{3}$ unit vector. Thus, PAN molecules were commensurate with the Au(111) substrate, as the model in Fig. 1d portrays.

Transformation from straight to meandering PAN molecules at 0.7 V. We first deposited a half monolayer PAN molecules on the Au(111) electrode at 0.95 V. The potential was then switched to 0.7 V from 0.95 V, resulting in dramatic changes of PAN's conformation from straight chains to meandering threads, as revealed by Fig. 2. To ensure the changes in structures arising from an alternation of potential and to see how fast the change would occur, we acquired a composite STM image (Fig. 2a) by switching the potential abruptly from 1.0 to 0.6 V as the tip was rastering downward to 1/3 of the frame. Initially linear PAN chains seen in the upper 1/3 of the frame turned crooked rapidly upon this shift of potential. This is not an imaging artefact, because changing the potential of the tip would not produce this kind of result. Neither did it come from some redox process, because dramatic as it appeared in the STM, this process should have registered in the voltammogram. Despite the poorly-defined molecular shape, PAN molecules were still long and independent entities, indicating that the backbone of PAN remained intact and no cross-link.

The internal molecular structure of meandering PAN threads was also discerned by high resolution scan, as Fig. 2b illustrates. Each PAN molecule was again imaged as chained protrusions, ascribable to the aromatic rings in PAN molecule. Not all protrusions exhibited the same corrugation heights; they differed by 0.2 ~ 0.4 Å. The shortest spacing between two neighbouring chains was 7 Å at 0.7 V, as compared to 10.4 Å observed for linear PAN at $E > 0.9$ V.

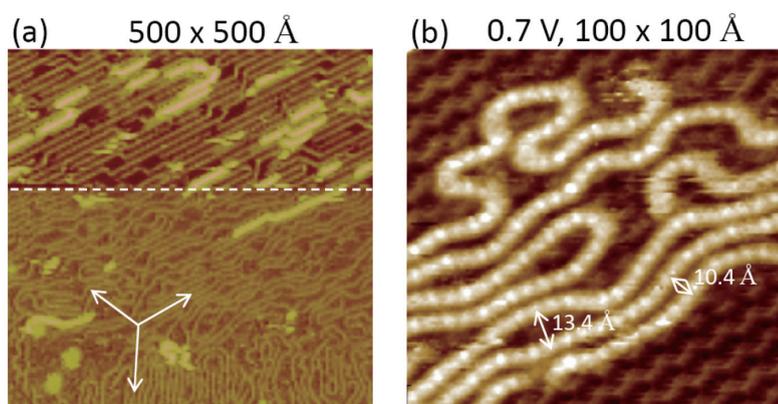


Fig. 2: In situ STM images (a) showing the instantaneous changes of molecular conformation as the potential was stepped from 1.0 to 0.6 V. The molecular resolution STM scan shown in (b) reveals the internal molecular arrangement of PAN molecules. The arrows in (a) mark the direction of main axis of the Au(111) substrate. The ordered pattern seen in the background is the $(3 \times 2\sqrt{3})$ -aniline adlattice.

XPS and NEXAFS. The high resolution N(*1s*) XPS spectra for PAN/Au(111) samples emersed at 1.0 and 0.5 V are shown in Fig. 3, revealing two distinct peaks at 399.3 and 401.4 eV in both cases. These features are ascribed to benzenoid-amine and nitrogen cationic radical, as reported by others. The relative intensity of these two peaks is almost identical, which implies that both samples were essentially emeraldine salts. If PAN were oxidized to pernigraldine at 1.0 V, the XPS spectra should have shown a single N(*1s*) peak at 398.4 (quinonoid-imine) due to the fully oxidized form or a pair of peaks at 389.4 (quinonoid-imine) and 402.5 eV (protonated quinonoid-imine). In fact, none of these features has ever been observed for PAN sample prepared by anodization at 1.0 V.

As Fig. 3 shows, the XPS spectrum for the 1.0 V sample contains less radical cation at 401.4 eV than benzenoid

amine at 399.3 eV. As the potential is changed from 1.0 to 0.5 V, one might expect more of the reduced benzenoid-amine at 399.3 eV. However, this is opposite to what was observed at 0.5 V, as the XPS signal at 399.3 eV for benzenoid-amine became even smaller than that of 1.0 V. It is likely that PAN molecules changed their conformation at 0.5 V in a way that raised the nitrogen radical-cation to a higher plane than that of 1.0 V. A larger signal at 401.4 eV is the result.

To further scrutinize the structures of the PAN/Au(111) interface, we used angular dependent XPS to probe the relative position of species contained in the PAN films prepared at 1.0 and 0.5 V. XPS spectra were collected at two emission angles, the normal and grazing emission angles, where electrons collection angles are 90° and 30° from the surface, respectively. The latter

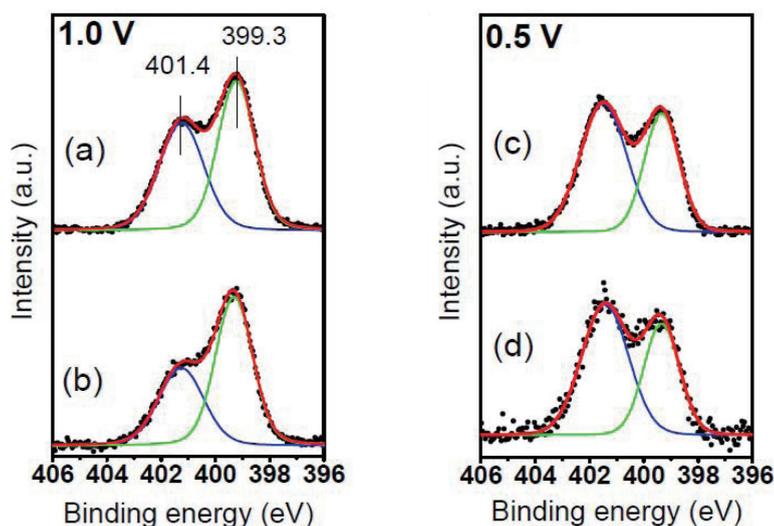


Fig. 3: High resolution N(*1s*) XPS spectra together with the least square fitting results for 3 Å PAN on Au(111) at 1.0 V (a and b) and 0.5 V (c and d) detected in normal emission geometry with a take-off angle of 90° (a and c) and grazing emission geometry with a take-off angle of 30° (b and d).

measurement is more sensitive toward chemical species located farther away from the Au(111) electrode. At 1.0 V the signal at 401.4 eV due to the radical-cation is reduced significantly at the grazing angle, while that of 0.5 V remains unchanged. These results show unambiguously that benzenoid - amine groups were located farther away from the Au(111) electrode than cationic nitrogen radicals at 1.0 V; whereas at 0.5 V the radical-cation and the benzenoid - amine distributed uniformly. The location of the adsorbed (bi)sulfate counter anion at the Au(111) electrode was similarly examined. At 1.0 V the ratio of the peak area for the N(1s) and S(2p) peak was 2.62 and 2.5 at normal and grazing emissions respectively, whereas they were 2.4 and 4.06 found with Au(111) at 0.5 V. These results indicate that the co-adsorbed (bi)sulfate anions repositioned themselves in response to the modulation of potential.

Experimental Station

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