

Real-time STM Imaging of the Reversibility of
Polyaniline's Conformation in response to Potential
Modulation of Au (111) Electrode

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Polyaniline (PAN), one of the famous conducting polymers, continues to draw interest from a wide spectrum of research disciplines ranging from electrochemistry to material science. The recent upsurge in studying polyaniline is fueled by the development of new characterization methods and procedures to control nanomaterials that are potentially useful in fabricating sensors, batteries, and probes in biotechnology.[1-3] Probing the size, molecular structure, and conformation has been an important issue because these microscopic characteristics can influence the macroscopic properties of polyaniline. From the perspective of interfacial structure, the adsorption of organic molecules on substrates has been the key to unraveling many interfacial processes.

We have performed more studies to explore how the structures of PAN molecules electropolymerized on Au(111) electrode varied with the chemical compositions. In particular, results were obtained in sulfuric, perchloric and benzene sulfonic acid.[4,5] STM imaging revealed that electropolymerization of aniline in sulfuric acid could be an surface event, yielding linear PAN molecules lying flat on Au(111) electrode. It is found that PAN molecular structure varied greatly with the applied potential at the Au(111) electrode. For example, PAN molecules assumed linear form at $E > 0.8$ V [vs. reversible hydrogen electrode (RHE)], but become clearly crooked at lower potential. A number of issues concerning this conformational change are not resolved yet. For example, it is not clear if this change is reversible to the modulation of potential, and the role of anion involved in this event. Here, we used in situ STM to study if the structural change was reversible to the potential modulation in nitric, sulfuric and perchloric acid, respectively.

The real-time STM imaging experiment was performed by generating a monolayer of PAN on the Au(111) electrode in sulfuric acid. As reported, PAN molecules assumed well-defined linear shape at $E > 0.8$ V in sulfuric acid, perchloric acid, etc. Shifting the potential from 0.8 to 0.6 V would cause fast changes of PAN structure into crooked forms. To see if this change was reversible to the change of potential, we switched the potential from 0.6 back to 0.8 V and conducted STM imaging to trace the subsequent changes. Obtained results showed that setting the potential at 0.8 V resulted in unlike changes of the PAN structure, depending on the chemical compositions of the electrolyte. The STM image shown below **Figure 1** was obtained in 0.5 M nitric acid containing 30 mM aniline. This STM scan comprises two sections with the upper and lower halves showing PAN molecules at 0.6 and 0.8 V, respectively. It appears that nearly all PAN molecules restored linear conformations at 0.8 V with only ~10% of PAN molecules stayed poorly defined states.

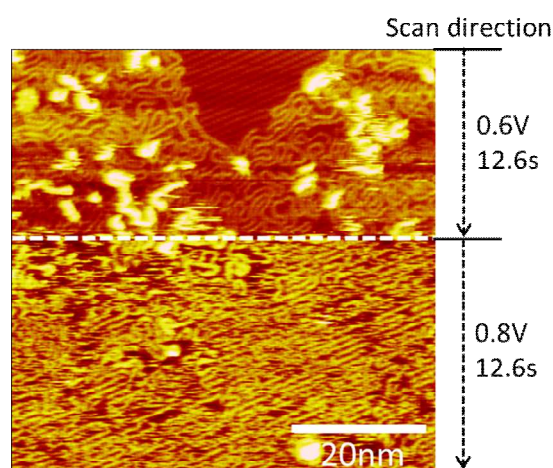


Figure 1. Potential-dependent in situ STM images showing changes in the molecular conformations of PAN admolecules supported by Au(111) in 0.5M HNO₃ solution containing 30 mM aniline.

Results were obtained to address the potential and anions effects on the conformations of PAN electrochemically formed on Au(111). Overall, the degree of reversibility in the PAN structure followed the order is HNO₃ > HClO₄ > H₂SO₄, according to molecular resolution STM images to be presented in this study. It is proposed that this result corresponds to the lyophilicity of these anions, which was important to guide their interactions to PAN molecules.

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