Potential-controlled Conformational changes of Polyaniline electrochemically deposited on Au (111) Electrode

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Abstract

In situ scanning tunneling microscopy (STM) was used to study the conformation of polyaniline (PAN) electrochemically deposited on Au(111) electrode in nitric, sulfuric, perchloric, and hydrochloric acids. As the potential was modulated between 0.8 and 0.6 V (vs. reversible hydrogen electrode), PAN molecules changed their oxidation states back and forth between the nigraniline and emeraldine states, which assumed linear and winding conformations. This potential - driven change in molecular conformations was fast and reversible in nitric acid and perchloric acids, but was largely irreversible in sulfuric acid. This contrast resulted from unlike interaction strength between anions in these acidic electrolytes and PAN molecules. PAN chains produced in nitric acid were softer than those formed in sulfuric acid, which manifested in the defects formed in these two electrolytes. Much more U-turns and crossings of two PAN chains were observed with PAN molecules produced in nitric acid. This unlike response of molecular structures to potential modulation also resulted in notable difference in the redox chemistry observed with cyclic voltammetry performed in these two electrolytes.

References

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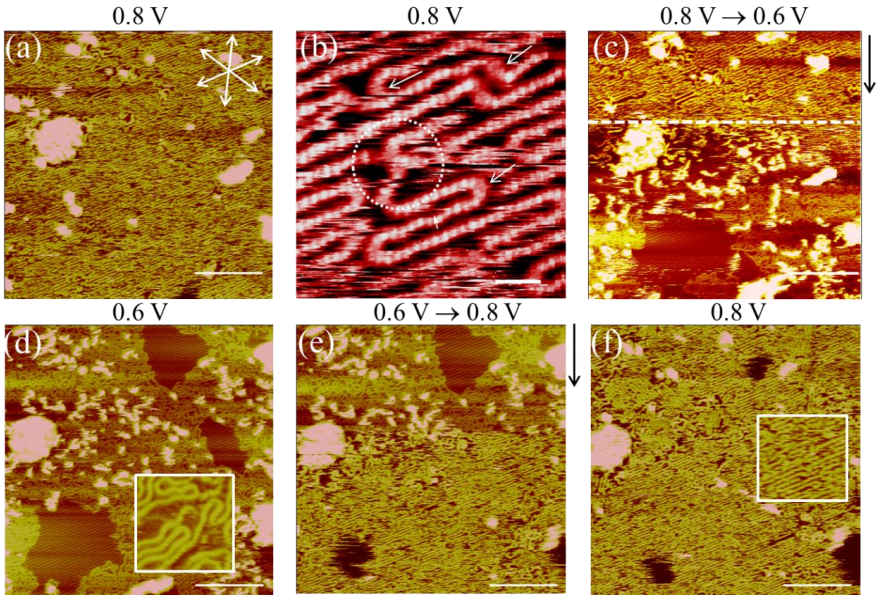

In situ STM images collected with an Au(111) electrode at 0.8 V (a and b) and 0.6 V (d) in 0.5 M HNO_3 containing 30 mM aniline. Panel (c and e) are composite STM images showing rapid changes of the PAN film in response to the shift of potential from 0.8 (0.6 V) to 0.6 (0.8) V at points indicated by the dotted lines. Arrows and dotted circles marked in (b) indicate loop and crossing defects in PAN molecules. Switching the potential from 0.6 to 0.8 V restored linear PANs seen in panels (e) and (f)). Scale bars = 20 nm.