In Situ STM Elucidation the Adsorption and Polymerization of Alkyl Ring-substituted Aniline on Au(111) Electrode

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Polyaniline (PANI) has been extensively examined for more than 40 years, which has led to a wide range of applications, including batteries, catalysis, corrosion protection, electrochromic devices, light-emitting devices, sensors etc. One of the notorious deficiencies of PANI is attributed to its poor solubility in the commonly used organic solvents, which can cause difficulties in processing PANI into practical devices. One of the tactics used to bypass this drawback has been the introduction of organic substituent(s) in the benzene ring of aniline. For example, a number of studies reveal that polymers produced from 2- or 3-alkylaniline are more soluble in tetrahyrofuran and chloroform than PANI.

We have employed cyclic voltammetry and in situ scanning tunneling microscopy (STM) to examine the adsorption of 3-methylaniline (3-MA) and 3-ethylaniline (3-EA) on Au(111) single-crystal electrode in 0.5 M H_2SO_4 + 0.03 M 3-MA or 0.03 M 3-EA. 3-MA admolecules were adsorbed in $(5 \times 2\sqrt{3})$rect at E > 0.5 V (vs. reversible hydrogen electrode), which restructured slowly into two less compact structures characterized as $(5 \times 2\sqrt{3})$rect and $(3\sqrt{3} \times 2\sqrt{3})$ upon raising potential to 0.8 V. In contrast, 3-EA formed a highly ordered $(4 \times 2\sqrt{3})$rect structure at the onset potential (0.8 V) of electropolymerization. All of these highly ordered structures featured alternating zigzag chains of 3-MA or 3-EA admolecules and bisulfate anions aligned in the <121> directions of the Au(111) substrate. 3-MA and 3-EA were oxidized and subsequently polymerized at 0.8 V, yielding linear polymer chains aligned preferentially in the <121> directions. These well-defined linear polymer chains were made possible by the ordered molecular templates described above. In situ STM imaging illustrated that linear polymer chains continued to thrive with time and grew into multilayer molecular films for 3-EA. In contrast, subsequent oxidative polymerization of 3-MA at E > 0.85 V produced poorly-defined polymer chains distributed uniformly on the electrode surface.

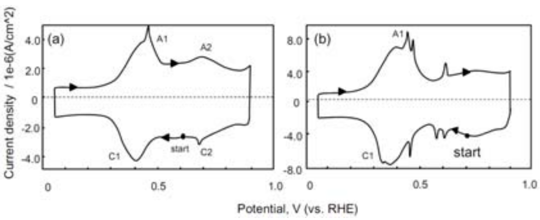

Fig. 1: Steady-date cyclic voltammograms recorded at 50 mV/s with Au(111) electrode immersed in 0.5 M H_2SO_4 and 6 mM 3-methylaniline (a), 3-ethylaniline (b).

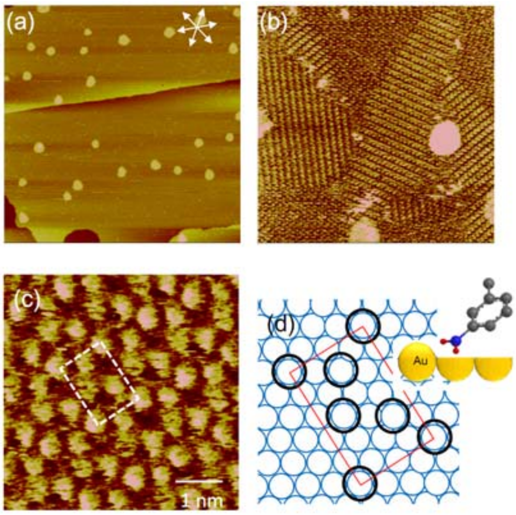

Fig. 2: In situ STM images with successively finer resolution acquired on Au(111) electrode at 0.5 V in 0.5 M H_2SO_4 and 6 mM 3-methylaniline (3-MA). The rectangle marked in (c) represents the unit cell of the $(5 \times 2\sqrt{3})$ structure which is explained by the ball model shown in (d). 3-MA admolecules are likely adsorbed in a tilted configuration, as shown in (d). The bias voltage and feedback current were set at -0.2 V and 1 nA, respectively.

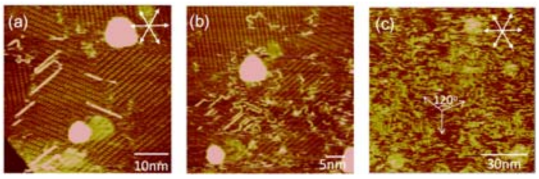

Fig. 3: In situ STM images showing the electropolymerization of 3-MA on Au(111) electrode in 0.5 M H_2SO_4 and 6 mM 3-methylaniline. The potential was set at 0.8, 0.85, and 0.9 V for (a), (b), and (c), respectively. Linear polymer chains were observed at the very beginning of polymerization at 0.8 V, followed by mostly crooked polymer chains produced at more positive potentials. The bias voltage and feedback current were set at -0.2 V and 1 nA, respectively.

References

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