In situ STM studies of 4,4'-bipyridine adsorption at Bi(111) electrode: influence of SO_4^{2-} concentration in supporting electrolyte.

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Impedance spectroscopy, *in situ* STM [1] and surface – enhanced infrared adsorption spectroscopy (SEIRAS) methods have been used for investigations of the 4,4'-bipyridine (4,4'-BP) adsorption at the electrochemically polished Bi(111) electrode from 0.5 M Na_2SO_4 and weakly acidified Na_2SO_4 pH ≈5.5÷6.0 supporting electrolyte solutions. In the region of maximal adsorption, the capacitance depression in the differential capacitance versus electrode potential curve has been observed, depending on surface inactive electrolyte solution. Based on the electrochemical analysis of impedance data, the heterogeneous adsorption and diffusion steps are the rate determining stages for 4,4'-BP adsorption at the Bi(111) electrode.

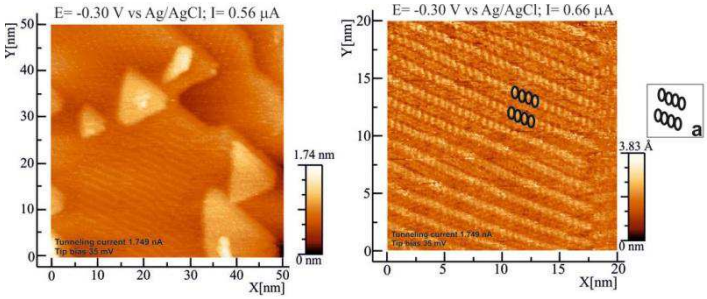

Figure 1. Unfiltered *in situ* STM images of 4,4'-BP adsorbed on Bi(111) | + 0.5 M Na_2SO_4 + 3*10^{-4} M H_2SO_4 aqueous electrolyte. (a) proposed packing model for 4,4'-BP molecules.

It was found that in 0.5 M Na_2SO_4 at electrode potential E = - 0.3V (vs Ag|AgCl in sat. KCl) 4,4-BP is forming a stripe pattern (Fig. 1) on Bi(111) consisting of two types of alternative rows, like it was found in the case of Au(hkl) and Ag(hkl) electrodes [2-5]. Wandlowski et al. proposed that the new formed 4,4'-BP adlayer consists of: 1) anisotropic, translational domain boundaries; and 2) rotational domain boundaries with characteristic angle [2].
Differently for ten times diluted Na_2SO_4 (0.05 M) solution, adsorbed 4,4'-BP forms less compact layer, but it is still in a form of a stripe pattern, as shown in Fig. 2. This type of the behaviour is explained by the sulphate coadsorption effect, $E \geq$ -0.5V, previously

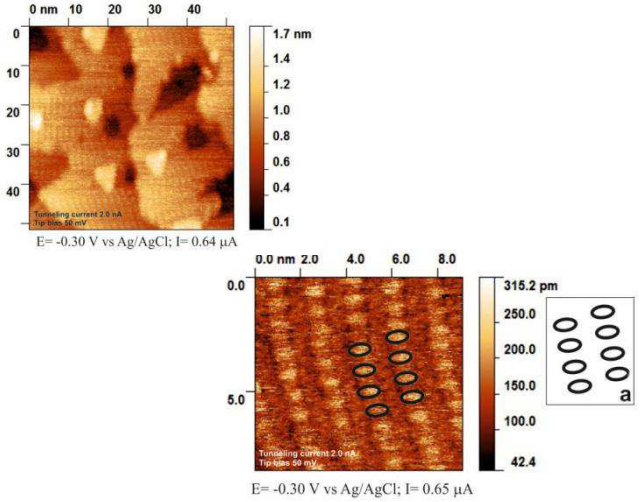

Figure 2. Unfiltered *in situ* STM images of 4,4'-BP adsorbed on Bi(111) | + 0.05 M Na_2SO_4 + 3*10^{-4} M H_2SO_4 aqueous electrolyte. (a) proposed packing model for 4,4'-BP molecules.

reported for camphor and 2,2'-bipyridine molecules adsorbed at Bi(111) studied by our group earlier [1].
The cyclic voltammograms for 0.5 M Na_2SO_4 + 4,4'-BP solution at Bi(111) demonstrate that at lower concentrations the adsorption process of 4,4'-BP is nearly reversible. However the electrochemical process at higher 4,4'-BP concentrations and $E \leq$ -0.5V is quite irreversible which is probably caused by the reduction of 4,4'-BP in two steps (electron transfer mechanism) and future formation of compact adsorption film on the electrode surface [3-5].

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