Porphyrin layers at metal-electrolyte interfaces: EC-STM and CV study

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Abstract: Porphyrin derivatives play a crutial role in biochemical processes like chlorophyll in the photosynthesis of plants, heme of red blood cells in the transport and storage of oxygen, and vitamin B-12 in the metabolism of creatures. Porphyrin derivatives are materials for electrocatalysts, drug production and cancer chemotherapy, sensors, solar cells, optoelectronic, data storage devices, and molecular electronics. We used electrochemical scanning tunneling microscopy (EC-STM) [1,2] and cyclic voltammetry (CV) to investigate these organic compounds at solid-liquid interfaces [3,4]. In particular the coadsorption of porphyrin molecules (TMPyP: Tetra(N-methyl-4-pyridyl)-porphyrin), sulfate and copper on Au(111), as well as iodine on Au(111), Au(110), and Au(100) was investigated with atomic resolution. With decreasing electrode potential the following sequence of phases was found: $\left(\sqrt{3}\times\sqrt{7}\right)R19.1°-SO_4^{2-}$ on Au(111)-(1×1), disordered SO_4^{2-}-layer on Au(111)-(1×1), $\left(\sqrt{3}\times\sqrt{3}\right)R30°$ coadsorption structure of 2/3 ML Cu and 1/3 ML SO_4^{2-}, 1 ML Cu covered by a layer of mobile SO_4^{2-}, a coadsorption layer of disordered porphyrin molecules and still mobile SO_4^{2-}, overpotentially deposited Cu-multilayers terminated by the Moiré-type $\left(\sqrt{3}\times\sqrt{7}\right)R19.1°-SO_4^{2-}$ structure [5-8] and covered by a dense layer of flat lying TMPyP molecules showing a growing square and hexagonally ordered arrangement, and at even more negative potentials and low Cu concentrations in the solution a pseudomorphic Cu-monolayer covered by a $\left(\sqrt{3}\times\sqrt{7}\right)R19.1°-SO_4^{2-}$ layer and ordered porphyrin layer on top [9]. The formation of CuTMPyP-metalloporphyrins and the Cu-Au alloy at multilayer copper deposits is suggested. The growth of long-range ordered two dimensional porphyrin layer was found on iodine precovered Au(111) and Au(100) [10]. STM images reveal planar adsorption of molecules. High resolution images reflect ligands and empty molecular cores. Tunneling at different bias voltages enabled to reveal the orientation of porphyrins with respect to the crystalline electrode.

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