Dynamics of Porphine Molecules at Electrochemical Interfaces by Time-Resolved STM

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Optimal control of surface self-assembly processes requires a thorough understanding of the dynamics of competing surface phenomena. We report the potential dependence of growth, dissolution, diffusion and phase transition processes involving self-assembled molecular structures. We seek to understand the electrochemical factors governing the dynamics of these processes. We have studied a free base porphyrin derivative, TPyP (5,10,15,20 -(4-pyridyl)-21H,23H-porphine) on Au(111) using high resolution electrochemical STM. STM is able to follow the growth of ordered domains in real time (Fig 1). The adlayer structure is highly potential dependent. At positive potentials (>0.5V_{SCE}), the Au(111) electrode can only adsorb a disordered layer of TPyP (Fig.2 A, top half). STM images showed that isolated molecules are immobile. At –0.1V_{SCE} cyclic voltammetry suggests the presence of molecules on Au(111). However, STM can no longer resolve the molecules (bottom half of Fig. 2 A), suggesting enhanced mobility of adsorbates. At intermediate potentials, the TPyP form a highly ordered adlayer (Fig. 2 B). Self-assembly of TPyP at electrochemical interfaces requires optimal molecule-substrate interaction. While chemical modification of the electrode surface, e.g., using an iodine adlayer on Au and Ag electrodes, to control the molecule-substrate interaction has been employed in the past, our results suggest a more convenient method, utilizing electrode potential to modulate the binding energy, to achieve a highly ordered adlayer.

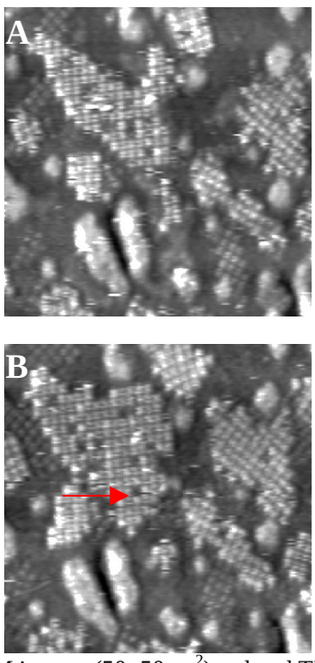

Fig 1 A) STM images (50×50nm^2) ordered TPyP molecular domain growth on Au(111) under 0.1M H_2SO_4. 0.1V_{SCE}. **B)** at 0.1V_{SCE} 6 minutes after acquisition of A. Defects in domains are clearly seen (arrow).

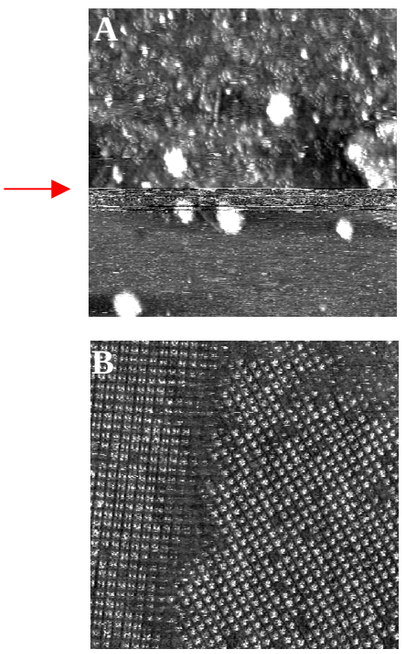

Fig. 2 STM images (50nm×50nm) of TPyP on Au(111) under 0.1M H_2SO_4. **A)** Potential originally at 0.5V_{SCE} (upper half of image) then stepped to –0.1V_{SCE} at the position of the red arrow. **B)** Ordered TPyP at –0.05V.