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Molecular Assembly of Hemin on Single-Crystal Au(111)-electrode Surfaces

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ABSTRACT

Iron porphyrin, hemin, is the active core in cytochromes, haemoglobin and myoglobin, and enzymes such as the peroxidases. These metalloproteins are engaged in respiratory electron transfer, oxygen transport and storage, and enzyme catalysis in the biosynthesis of a range of metabolites. Hemin itself also acts as catalyst in electrochemical reduction of dioxygen and other small inert molecules such as nitrogen monoxide, and in electrochemiluminescent detection of dioxygen, peroxide, DNA, and proteins [1, 2].

Л-Л interactions of hemin with carbon materials have been broadly studied [3]. Hemin on noble metal surfaces has been prime targets in high-resolution STM [4] but much less used in applied contexts such as biosensors and drug delivery. How hemin molecules interact with noble metal surfaces offers, however, other challenges in nanoscale and single-molecule science. We have studied hemin adsorption on well-defined single-crystal Au(111)-electrode surfaces using electrochemistry combined with scanning tunnelling microscopy under electrochemical control. Hemin gives two voltammetric peaks assigned to adsorbed monomers and dimmers (Fig. 1A). *In situ* STM shows that hemin self-assembles in ordered monolayers through non-covalent adsorption, as the reconstruction of the Au-(111) surface underneath the hemin layer is clearly visible (Fig. 1B).

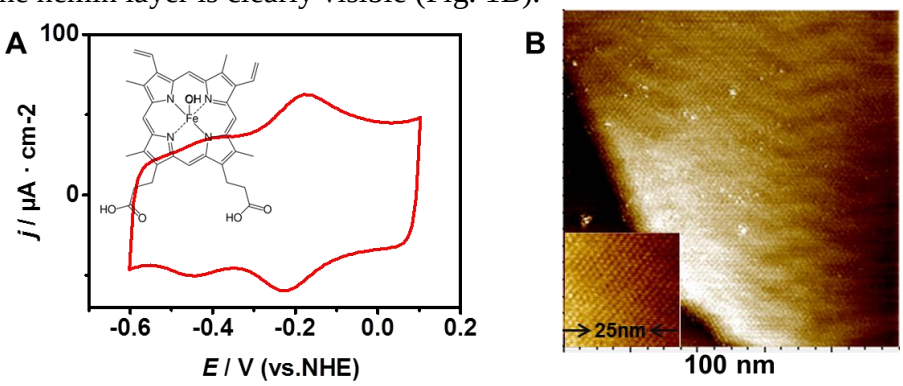

Fig. 1. (A) Voltammogram of hemin modified single-crystal Au(111)) electrode in NaOH solution, pH 11.9. Scan rate, 3 V/s. (B) *In-situ* STM of hemin modified Au(111) electrode surface in NaOH solution, pH 11.5. E_{sample}, 0.20 V, E_{tip}, 0.06 V vs. NHE. 100 × 100 nm^2.

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