Nanoscale conductance imaging of electronic materials and redox proteins in aqueous solution

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Electron Transfer (ET) plays essential roles in chemistry and biology, as it is involved in electrochemical reactions and in crucial biological processes such as cell respiration and photosynthesis. ET takes place between redox proteins and in protein complexes, and it displays an outstanding efficiency and environmental adaptability. Although the fundamental aspects of ET processes are well understood, more experimental methods are needed to determine electronic pathways, especially in complex systems like organic and inorganic nanostructures as well as in biomolecules like nucleic acids and proteins. Understanding how ET works is important not only for fundamental reasons, but also for the potential technological applications of these redox-active nanoscale systems.

Electrochemical Scanning Tunneling Microscopy (ECSTM) is an excellent tool to study electronic materials and redox molecules including proteins[1]. It offers atomic or single molecule resolution and allows working in aqueous solution, in nearly physiological conditions in the case of proteins, and under full electrochemical control. Beyond imaging, ECSTM allows performing current-voltage and current-distance tunneling spectroscopy. We have adapted this spectroscopy mode of ECSTM to include a sinusoidal voltage modulation to the STM tip, and current measurement by means of a lock-in amplifier, which renders a signal that is proportional to the differential conductance dI/dV of the studied surface[2]. We have used this setup to record for the first time spatially resolved, differential conductance images under potentiostatic control (differential electrochemical conductance (DECC) imaging). We have validated and optimized the technique using an iron electrode, whose reversible oxidation in borate buffer is well characterized[3] (Figure 1).

We have applied DECC imaging to gold Au <111> surfaces coated with *P. Aeruginosa* Azurin, a redox metalloprotein with a copper center involved in the respiratory chain of denitrifying bacteria. Azurin can be immobilized on single crystal Au <111> surfaces via a dithiol covalent bond, and it has become a model system to study biological ET processes[4]. DECC imaging provides simultaneously the surface topography and local conductance with a resolution of a few nanometers, and reveals regions with different conductance within the protein. The characterization of conduction pathways in redox proteins at the nanoscale would enable important advances in biochemistry and would cause a high impact in the field of nanotechnology[5]. This method can be used to study more complex biosystems, like multi-center redox proteins and protein redox complexes, and lead to a deeper understanding of their electronic properties and ET pathways.

References

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Figures

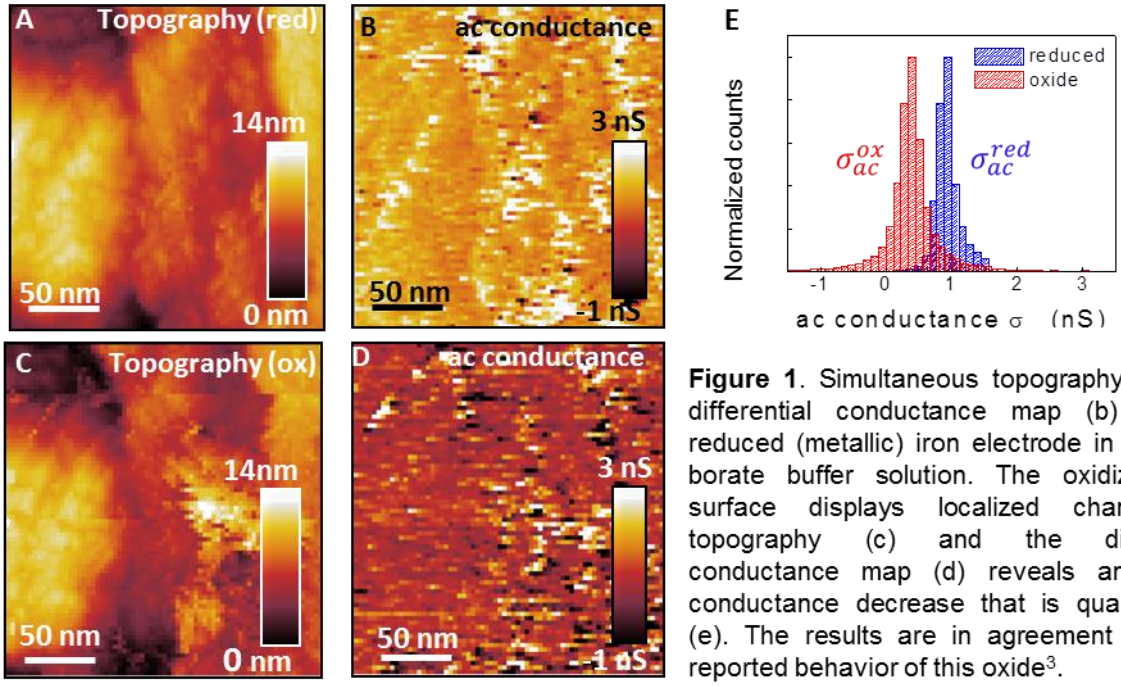

Figure 1. Simultaneous topography (a) and differential conductance map (b) of the reduced (metallic) iron electrode in aqueous borate buffer solution. The oxidized iron surface displays localized changes in topography (c) and the differential conductance map (d) reveals an overall conductance decrease that is quantified in (e). The results are in agreement with the reported behavior of this oxide[3].