Integrating Micro- and Nanoelectrodes Into Atomic Force Microscopy Cantilevers Using Focused Ion Beam Techniques

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The investigation and manipulation of surfaces at an atomic scale has been revolutionized by the introduction scanning probe microscopic (SPM) techniques. Complex analytical problems in material and life sciences demand complementary information on physical and chemical properties at the molecular level. Hence, combination of SPM techniques is the logical consequence.

Scanning electrochemical microscopy (SECM) uniquely provides *in-situ* electrochemical, chemical, and biochemical information on surfaces and interfaces. An ultramicroelectrode is scanned in the nearfield across the sample surface (solid or liquid). The surface properties of the substrate influence the electrochemical response of the ultramicroelectrode, providing information on the nature of the substrate. Due to the difficulty in positioning electrodes at the nanometer range, SECM offers limited lateral resolution compared to scanning tunneling (STM) and atomic force microscopy (AFM). In particular, the trend towards nanoelectrodes for enhanced spatial resolution and the use of micro/nanosensors as SECM tips demands innovative approaches for manufacturing and positioning the SECM probe.

The recent development of micro- and nanoelectrodes integrated into AFM cantilevers demonstrates a novel approach combining micro- and nanoelectrochemistry with AFM measurements. Frame- or ring-microelectrodes are integrated into standard AFM cantilevers by microfabrication techniques. Consequently, electrochemical processes can be imaged or induced at a nanoscale during simultaneous AFM measurements.

Chemical modification of the electrode surface with bioreceptors (e.g. enzymes) integrates (bio)sensing devices for enhanced molecular recognition and specificity.

This concept can be extended towards multifunctional scanning probes/sensors, combining e.g. SECM with AFM and scanning nearfield optical microscopy (SNOM) into a single tri-functional tip or integrating multiple electrode/sensor systems.

The production of SECM/AFM tips is entirely based on microfabrication processes. The main processing steps include deposition of the electrode material (60 – 100 nm) onto the cantilever surface by sputtering. In case of a conducting tip prior deposition of an insulation layer is required. Commonly used electrode materials include gold, platinum, and modified carbon. Subsequent insulation is achieved by chemical vapor deposition of silicon nitride, mixed silicon nitride/oxide or parylene.

Exposing the micro-/nanoelectrode in the required working distance to the sample surface is achieved by a 3-step focused ion beam (FIB) cutting/milling process. FIB is used to expose and shape the integrated electrode, and to control the working distance by remodeling of an insulating AFM tip.

In order to demonstrate full functionality, the featured integrated SECM-AFM tip was mounted in a standard atomic force microscope (Nanoscope III, Digital Instruments), equipped with a fluid cell. The whole instrument was located in a faraday cage and the electrochemical signal was detected by a bi-potentiostat (CH Instruments 832A). All images were obtained in the contact mode of the AFM.

As a model surface a porous poly-carbonate membrane with a thickness of 11 µm and an average pore size of 1 µm was coated with a layer of 50 nm gold on the bottom side.

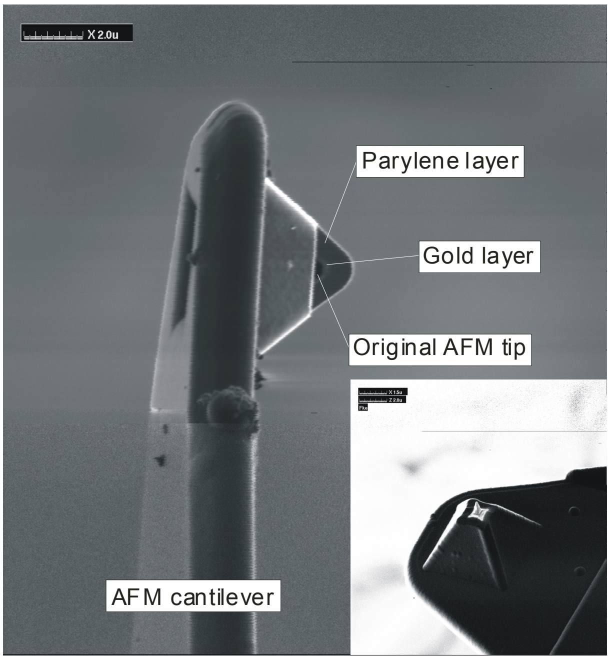

Fig. 1: FIB-image of an integrated SECM/AFM tip after first FIB cutting. Inset shows an integrated frame-nanoelectrode (bright square) with concentric re-shaped AFM-tip.

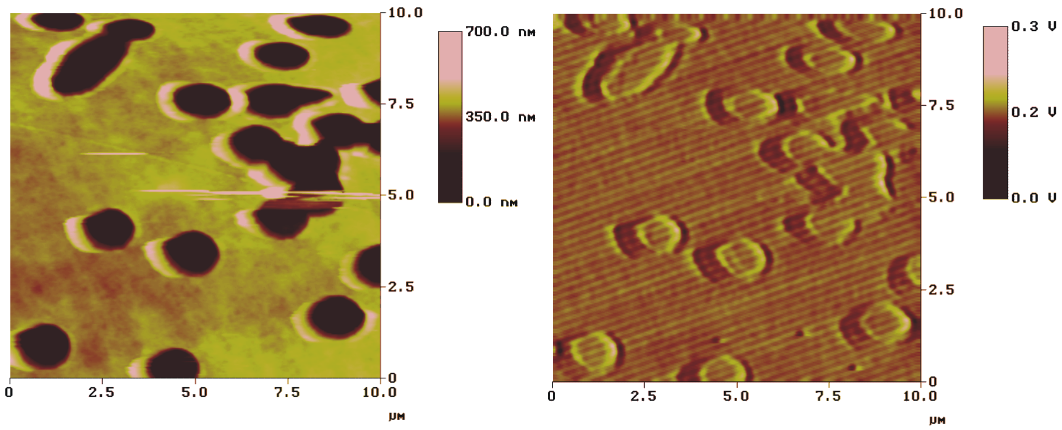

Fig. 2: Simultaneously recorded height and current images of a porous polymer membrane. (a) Top view of the AFM image and (b) top view of the simultaneously recorded current image. Redox mediator: 30 mM $Fe[CN]_6^{4-}$ in 0.5 M KCl electrolyte solution. Scan parameters: 2 Hz. Electrode edge length: 1 µm.