The geometry of nanometer-sized electrodes and its influence on electrolytic currents and metal deposition processes in scanning tunneling and scanning electrochemical microscopy

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Abstract

Electrodes with an effective radius of about 10 nm have been produced by a combination of electrochemical etching, electrophoretic deposition of polymer, and heat curing. Their size and stability were characterized by cyclic voltammetry. They were then used in combined electrochemical scanning tunneling microscopic (ECSTM) and scanning electrochemical microscopic (SECM) experiments. In an extension of an earlier report, electrochemical surface modification approaches are reported here. They comprise the local electrochemical removal of a self-assembled monolayer (SAM) of dodecanethiol on flame-annealed gold by an electrochemical desorption procedure. The possibility of local electrochemical deposition is demonstrated by positioning a nanoelectrode 0.5 nm above a surface and switching off the distance regulation while performing an electrodeposition of Pt at the tip. The growing deposit bridges the tip-sample gap. If the distance regulation is switched on after 1 ms, the Pt junction is disrupted leaving a Pt nanodot at the sample surface. The dot was characterized by ECSTM experiments after solution exchange. Digital simulations by the boundary element method (BEM) provide a quantitative description of Faraday currents in nanoelectrochemical assemblies. A software tool was created that can accept arbitrary geometries as input datasets. The flexibility of the simulation strategy was demonstrated by the calculation of local current densities during electrochemical copper deposition on a
smooth electrode in the presence of an ECSTM tip close to the surface. The current densities deviate less than 1% from those in the absence of tip if the average current density is kept below 1 µA cm⁻². SECM approach curves for nano-electrodes were also calculated.

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1. Introduction

The broad application of scanning probe techniques such as electrochemical scanning tunneling microscopy (ECSTM) and to a lesser extent electrochemical scanning force microscopy (ECSFM) has significantly contributed to the microscopic (atomistic) understanding of the reactivity of solid–liquid electrodes [1–5]. The most detailed images could be obtained for ion-transfer and phase formation reactions at single crystal noble metal electrodes [6]. Parallel to the advance of ECSTM, scanning electrochemical microscopy (SECM) was developed as a new tool for localized electrochemistry (see [7–15] for general reviews). It shares the scanning principle with ECSTM but it can be distinguished from it by an entirely different mode of action. The current is caused by the Faraday reaction at the probe electrode that converts dissolved species, often under diffusion-controlled conditions rather than by the tunneling effect in ECSTM. The reaction at the probe electrode can be coupled to electrochemical, catalytical or etching reactions at the specimen electrode via diffusing species. Therefore, the current depends on the heterogeneous reaction rates at the sample and at the probe as well as on the mass transport rate between the sample and the probe. As the experiments are carried out in a large excess of supporting electrolyte, the dominating mode of mass transport is diffusion which can be well described by continuum models based on Fick’s laws. Digital simulations of the related diffusion–reaction systems have therefore accompanied experimental investigations since the inception of SECM [16–25]. Because the diffusional transport is well understood, the heterogeneous reaction rate can be determined for a large variety of chemical reaction and mass transport phenomena at solid–liquid interfaces. Unlike in ECSTM, such investigations are also possible if all the reaction partners are dissolved and no topographic changes occur on the sample during the reaction. In order to accurately describe the mass transport phenomena in SECM, the geometry of the probe must be well known. Because of this and problems in preparation, disk-shaped ultramicroelectrodes (UME) with radius, \( r_T \) of 5–15 µm have been preferred for the majority of SECM studies. Such an electrode is moved in a working distance, \( d \), above the sample that corresponds to a few UME radii, i.e. several orders of magnitude larger than the tunneling distance used in ECSTM experiments.

Two imaging modes can be distinguished. In the generation-collection mode the bulk solution contains only the supporting electrolyte. The UME detects species generated at or released locally from the sample. In the so-called feedback mode⁴ one form of a quasi-reversible redox couple, i.e. the mediator, is added in millimolar concentration to the supporting electrolyte. The mediator is converted at the UME under diffusion-controlled conditions which produces a steady-state current, \( i_{T,\infty} \), if the electrode is positioned far away from any surface. However, if the UME is brought close to an inert and insulating surface, the diffusion of the mediator to the UME is blocked and the UME current \( i_T \) decreases below \( i_{T,\infty} \) (called negative feedback). If the UME is brought above a conductive surface or a catalytically active surface, \( i_T \) increases above the value found for an inert and insulating surface. The magnitude of this increase

⁴ Please note that unlike in ECSTM the term “feedback” in the context of SECM does not refer to an electronic mechanism that keeps the UME-distance constant. It refers to the interaction between the electron transfer reactions at the sample and the UME probe.
depends on the local reactivity of the sample. A diffusion-controlled reaction at the sample and the tip constitutes an important limiting case for which the term positive feedback is frequently used. Because of the defined geometry, $i_T$ can be calculated with a high precision by solving the diffusion equation numerically and considering the sample kinetics as boundary conditions. This quantitative rigor, the steady-state nature of many signals and the flexibility in the choice of electrochemical reactions have opened SECM to a very broad range of important applications. Examples of considerable practical importance include reactions at fuel cell catalysts, reactions preceding pitting corrosion [26–31], investigations of enzymatic reactions of living cells and biotechnological surfaces [32,33], and fundamental research of charge transfer at liquid–liquid interfaces [12]. The information thus obtained is complementary to the ECSTM results.

A good contrast can only be achieved in SECM if $i_T$ is substantially reduced over inert surfaces. This is best achieved by an electrode of disk-shaped geometry with an insulating shaft of some thickness. Traditionally such UMEs have been produced by sealing Pt wires into glass and exposing a cross-section by grinding and polishing. Because Pt wires are not available with diameters of less than 10 μm and because they would be extremely difficult to handle manually, such a technology is essentially confined to the micrometer size regime. Beside the technical problem of UME preparation and UME positioning, the larger working distance and the diffusional nature of the mass transport between sample and probe [34] are the principal limitations to the achievable resolution obtainable with SECM. It will always be much lower than in ECSTM.

However, the vast majority of SECM experiments are limited by the availability of small UME—also called nanoelectrodes—rather than by principal limitations. Currently, a wide variety of experimental approaches is tested in order to circumvent this problem. They include positioning the electrode in the tunneling mode, retracting it and measuring either a current transient at fixed position [35] or an image in a fixed plane above the sample [36,37]. Alternatively, microelectrodes have been integrated into more complex probes such as atomic force microscopy (AFM) cantilevers [38] or optical fibers for scanning near-field optical microscopy [39]. On the other hand, ECSTM studies are increasingly carried out at electrodes at which reactions such as deposition or dissolution take place and the results may be influenced by the diffusional mass transport in the solution phase. This applies both to imaging experiments [40] and local surface modifications [41].

Our group aimed to blend the capabilities of ECSTM and SECM thereby enabling SECM experiments in nanometer dimension with the goal of spatially correlated imaging of topography and local reactivity [42] as well as of exploring new possibilities for local electrochemical surface modification in the nanometer size regime. In parallel a new digital simulation tool was developed which is based on the boundary element method (BEM) that enables the analysis of local concentrations and fluxes in nanometer-sized electrochemical set-ups of complex geometry [43].

2. Experimental

2.1. Substances

Gold substrates (12 × 12 mm borosilicate glass, 2 nm chromium, 300 nm gold, Arrandee, Inc. Lienen, Germany) were flame-annealed to obtain atomically smooth terraces with predominately Au(111) orientation. Flame annealing was done by heating the gold layer until it glows red, leaving it 60 s in this state and cooling the sample in an Ar stream. This procedure was repeated 3 times. Chemisorption of dodecanethiol occurred during immersion of gold substrates into a 1 mM solution of n-dodecanethiol (Fluka, Deisenhofen, Germany) in 2-propanol (analytical grade, Merck, Darmstadt, Germany) for 24 h. Electrolyte solutions for imaging were prepared from deionized water (18 MΩ cm, Labostil, Christ, Stuttgart, Germany) and contained 0.1 M H₂SO₄ (analytical grade, Merck, Germany), 0.1 M Na₂SO₄ and 10 mM [Ru(NH₃)₆]Cl₃ (Strem, Newburyport, MA, USA).
2.2. Combined ECSTM-SECM instrumentation

The combined ECSTM-SECM instrument was built by modification of the commercial Discoverer 2100 TMX (Topometrix Corp., Santa Clara, CA, USA). This instrument was designed as a scanning force microscope with the scanner (either 1 × 1 × 0.8 μm³ or 70 × 70 × 10 μm³) attached to and placed underneath the sample. The STM head was placed above the open electrochemical cell and did not move with respect to the laboratory. A custom-built bipotentiostat (µBIP2, M. Schramm, Heinrich Heine University Düsseldorf, Düsseldorf, Germany) was connected to the external analog output (DA0 and DA1) and analog input (AD0, AD1) lines of the Electronic Control Unit (ECU) of the TMX 2100. The bipotentiostat included a preamplifier replacing the original preamplifier in the STM head. The operation of the whole setup was organized from an in-house developed software that makes use of routines contained in the SPMTool dynamic link libraries (DLL, Version 5.01, Topometrix) and own DLLs. This strategy allowed to control the hardware of the ECU and to design new experiments not contained in the commercial instrument control software. A more detailed description of the software is given elsewhere [42].

The bipotentiostat controlled a four-electrode cell with the working electrode 1 (WE1) being the ECSTM-SECM sample and the working electrode 2 (WE2) being the probe. A hydrogen-loaded palladium wire (PdHₓ, Ref) served as reference electrode (0.05 V vs. NHE for 0.03 < x < 0.57). All potentials in this work are given with respect to the saturated calomel electrode. The auxiliary electrode (AE) was a large platinum sheet attached to the inner perimeter of the electrochemical cell of TMX 2100. The solution exchange in the electrochemical cell was enabled by a pair of polymer tubes attached to the fixed ECSTM head and connected to a peristaltic pump. Special precautions were taken to prevent solutions from spilling out of the cell [42]. The concentration of a redox active species c could be decreased from the initial concentration c₀ by exchange against pure electrolyte according to c(t) = c₀ exp [-t/22.8 s] using an influx flow rate of 8.3 μl s⁻¹.

2.3. Probes

Combined ECSTM-SECM probes were made from Pt/Ir wires (90/10, 250 μm diameter, Goodfellow, Bad Nauheim Germany). The wire was inserted into two polymer tubes, 12 mm long, with 300 μm inner diameter. The tubes were arranged on the wire to have a gap of about 1 mm between them. This setup together with a Pt counter electrode was inserted into a solution of 100 ml water, 39 g KCN and 8 g NaOH in such a way that the gap between the tubes was just immersed. Caution: This solution should be handled in a fume hood free of acids to exclude evolution of HCN in case of spills. Electrochemical etching was achieved by applying a square wave voltage (8 V amplitude, 10 kHz) to the two-electrode setup. Etching was confined to the gap between the two polymer tubes and continued until the lower end of the wire fell off. After rinsing, the tips were coated with an anodic electrophoretic paint (Glasophor ZQ 84-3211, BASF, Ludwigshafen, Germany) as described by Bach et al. [44] by applying 25 V for 5 min in a two electrode setup. After rinsing with deionized water the electrodes were kept tip-up at 210 °C for 15 min in a drying oven. During that time the polymer cross-linked. Furthermore, the layer was disrupted at the very end of the tip and exposed a nanometer-sized area. The electrodes were characterized by cyclic voltammetry in typically 10 mM solutions of [Ru(NH₃)₆]Cl₃. From the sigmoidal cyclic voltammograms, the radius of a microdisk electrode, rₑₓ有效地 was calculated that would cause the same limiting current as the prepared tips.

\[ r_{ₑₓ有效地} = \frac{iₗₘₐₓ}{(4nFDc)}. \]  

(1)

The values for these effective radii varied between 3 and 400 nm. If needed, the procedure could be repeated until the desired cross-section was obtained.

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[5] Today, the company belongs to Thermomicroscopes within the Veeco group (Woodbury, NY, USA).
2.4. Simulation tools

Simulations with the BEM were performed by the in-house made software written in C++ on a Linux-PC with a 2 GHz processor and 512 MB memory capacity. Average computation time was about 2–3 min for a single geometric configuration of about 3000 mesh elements in the system and required 320 MB of memory. A whole image consisting of 25 × 25 data points could be calculated in 24 h. The following algorithms were used in the overall BEM setup: the Gauss-Legendre 13-point quadrature rules for numerical integration as well as analytical two-dimensional surface integration, the LU-decomposition for solution of dense linear systems and the Delaunay triangulation for composing the mesh. A separate geometry editor was created and used for a mesh development and assignment of boundary conditions to mesh elements.

3. Results and discussion

3.1. Nanometer-sized probes for scanning electrochemical microscopy

3.1.1. Influence of probe shape on SECM imaging

The preparation of amperometric electrodes smaller than 1 μm has been intensively over the last years. Several groups produced very small probes that enable combined scanning probe microscopies, e.g. a ring electrode around an optical fiber for SECM-scanning near-field optical microscopy [39], frame electrodes integrated into SFM cantilevers [38] or heptode microelectrodes [45]. Microdisc or microcone electrodes have also been produced [46–50]. Fig. 1a, geometry 1 shows a microdisc electrode. This shape is most frequently used in SECM imaging because the insulating shielding effectively blocks the diffusion of the mediator from the bulk solution when positioned close to a surface of interest. This is a prerequisite for achieving a good contrast in SECM imaging. A pointed cone, as preferred in ECSTM studies (Fig. 1a, geometry 6), cannot give a good contrast in SECM feedback imaging. This can be concluded from SECM approach curves calculated for electrodes of different geometries given in Fig. 1b using the boundary element method (BEM). The BEM approach will be shortly described in Section 3.3. The plot shows the calculated diffusion-controlled Faraday current at the UME, \( i_T \) as a function of the distance, \( d \), between the sample and the probe. The values are normalized to the diffusion-controlled current, \( i_{T,\infty} \), in the solution bulk (far from any sample surface) and to the effective radius of the probe, \( r_{T,\text{eff}} \). The qualitative result is very clear. No contrast can be achieved in SECM feedback imaging if the cone is very protruding. However, shallow cones show approach curves that do not deviate much from the behavior of a disk electrode (Fig. 1, curves 2, 3). We therefore aimed for the preparation of such electrodes. They should still allow ECSTM imaging although with lower resolution but could be used as reasonable functional probes for SECM imaging as well.

3.1.2. Electrochemistry with nanoelectrodes

We as well as others [46–50] have used a combination of etching of the metal wire with the electrophoretic coating of the wire followed by heat curing to expose a small active electrode area as introduced by Bach et al. [44]. The coating process gives reproducibly electrodes with sizes between 3 and 400 nm radius. A cyclic voltammogram of such an electrode is shown in Fig. 2a. The radius of 4 nm was determined as the effective radius according to Eq. (1) with \( D = 5.3 \times 10^{-6} \text{ cm}^2 \text{s}^{-1} \) [51] for [Ru(NH₃)₆]³⁺. In fact, the cyclic voltammogram agrees very well with that of a true microdisc electrode (Fig. 2b) produced by pulling a sealed platinum wire melted by a laser puller [52,53]. Unfortunately, these small electrodes are not suitable for combination with an ECSTM due to problems in mounting the tips. Furthermore the thick insulating shielding would prevent the tunneling contact to the sample as the mechanical probe-sample contact would most likely occur at the glass shielding of the probe.

While the reproducibility of the etching-and-coating procedure was quite satisfying, the stability of the electrodes remained an open issue. Qualitatively it was observed that the active
electrode area was often substantially increased after imaging experiments. A systematic study of the stability of electrodes was conducted. An electrode was subjected to repeated potential cycling in 10 mM [Ru(NH₃)₆]³⁺ solution and the diffusion limited current was taken as a measure of the electrode size (Fig. 3, inset). From the first cycle $r_{T,\text{eff}} = 40$ nm was calculated. Prolonged cycling showed a quite good reproducibility of the cyclic voltammograms. Only the cycles after 0, 12 and 17 min are shown in the inset of Fig. 3. Although no manipulation was done, the active electrode area started to increase after 22 min (Fig. 3, curve 4). After this time the electrode area grows within 15 min to the 37-fold of its original size (Fig. 3). This strange behavior explains not only that successful imaging experiments could be performed using such electrode [42] but also that an increase of the electrodes is often observed during experimentation. We assume that the state of the electrode after heat curing with a very small opening in the thin polymer film represents a metastable state. The morphology of the polymer film may change, particularly if the transfer from air to an aqueous solution changes the interfacial energies at the various interfaces. It seems that the change

Fig. 1. (a) Schematic representation of electrodes with the shape of a microdisc and rounded conical electrodes with different ratios of cone height $h$ to base radius $r$: (1) 0, (2) 0.3, (3) 0.6, (4) 0.87, (5) 2.0, (6) 10.0. (b) Calculated normalized approach SECM for electrode geometries (1) to (6).
of the polymer film, once initiated, can be rapid on
the timescale of conventional ECSTM and SECM
experiments.

3.1.3. SECM experiments with nanoelectrodes

The described electrodes have been used in a combined SECM-ECSTM instrument. The combined imaging used an ECSTM line scan to acquire topographic information. Then the tip-sample distance was increased to 20–50 nm and the tip potentials switched in order to drive electrochemical reactions. The tip was then moved parallel to the surface back to the starting point while recording the Faraday current (Fig. 4). This setup was used with nanoelectrodes produced by etching and electrophoretic coating in order to record approach curves to self assembled monolayers (SAM) of alkanethiolate on flame-annealed gold. The approach could be performed until a tunneling contact was established. In this situation the tip penetrated into the alkanethiolate film and mechanically disturbed it [42]. Upon retraction the disturbance became evident, because the film lost its inhibiting properties. When the retraction was interrupted for 60 s to allow relaxation of the film, the inhibiting properties were regained [42].

The combined ECSTM-SECM imaging mode was tested on alkanethiolate-covered surfaces into which defects of $100 \times 100 \text{ nm}^2$ had been introduced by mechanical abrasion (Fig. 5) [42]. There was no notable change in topography as seen by ECSTM before and after the modification (Fig. 5a and c) because the thickness of the alkanethiolate film was low compared to the roughness of the gold electrode in the image frame. The tip penetrated into the organic film during the ECSTM part of the experiment so that increased

![Fig. 4. Schematic of the combined SECM-ECSTM imaging experiment.](image)
currents were observed above the entire monolayer in the SECM part of the experiment (Fig. 5bandd). In the two areas where mechanical abrasion was performed, the monolayer was irreversibly damaged. This resulted in higher SECM currents after the modification (Region I and II in Fig. 5d). The signal width was larger than the damaged region of the SAM. This was seen as a consequence of a non-linear convolution of geometries of the modified sample area and the probe electrode in this experiment. The region III in Fig. 5d also shows enhanced currents. This corresponds to a defect marked with III in Fig. 5c, which was unintentionally created probably by a mechanical collision between the tip and the sample when moving the tip between different image frames.

3.2. Local electrochemical surface modification in the nanometer scale

3.2.1. Local electrochemical desorption

Over the last years we introduced an electrochemical procedure by which defined regions of a SAM can be desorbed when an ac current is applied between a macroscopic thiolate-covered gold electrode and a microscopic tool electrode positioned 10 μm above the specimen surface over a period of 30 s [54–56]. Extensive experiments in the micrometer range showed that desorption commences directly underneath the UME [54]. The confinement of the desorption is due to the increased capacitance of the sample regions from which the SAM was removed. In the kHz frequency range the currents are mainly charging...
currents which have to be balanced by a microscopic counter electrode. This is only possible if the bare regions of the sample have about the same size as the tool electrode [55]. Attempts were made to adapt this procedure to the nanometer-size regime. A nanoelectrode produced by etching and electrophoretic coating was brought into tunneling contact with a flame-annealed Au sample coated with a dodecanethiolate SAM and immersed into an electrolyte. The probe was then positioned above the area to be modified followed by retraction of 50 nm from the surface and application of an ac voltage of 5 kHz and 200 mV (RMS) for 1 s (Fig. 6a). The resulting structure was imaged in an ECSTM experiment and is shown in Fig. 6b. A region with a radius of about 14 nm was modified. However, the modification is not restricted to the SAM. A pit of 1.9 nm depth was formed (Fig. 6c). This value is of the same order of magnitude as the thickness of the dodecanethiolate SAM. However, the tip penetrated into the alkanethiolate film under the experimental conditions in the ECSTM imaging. Fig. 6c gives the profile of the gold surface and indicates that the topmost gold atoms were removed during this procedure. It is most likely that this also occurred during the earlier experiments in the micrometer range but was not detected due to the lower resolution of conventional SECM experiments. For modifications in the micrometer range the depth of the pit is also not very significant because the topographic change is negligible compared to the roughness of polycrystalline gold electrode used for such experiments. The experimental parameters of the desorption protocol were varied in order to explore different effective voltages, working distances and desorption times. The latter had to be shorter than 1 s. Otherwise larger structures were formed having diameters of up to 5 μm. More seriously, the active area of the tip electrode was changed and material was deposited on the sample with some parameters sets. This remarkably contrasted with the experiences in the micrometer scale where electrodes sealed in glass could be used for multiple modifications and results were not sensitive to small variations of experimental conditions [55]. Therefore, mechanical abrasion of the alkanethiolate films during small-area ECSTM scans was preferred for local removal of alkanethiolate SAMs (vide supra).

3.2.2. Local electrolytic deposition of Pt nanodots

The local electrochemical deposition of nanodots is inspired by a procedure reported by Li and Tao [57] for the observation of quantum transport in copper nanowires. In our work local electrochemical deposition was used to form an isolated Pt nanodot as an example of a catalytically active metal on dodecanethiolate-covered flame-annealed gold as representing an electrochemically inert surface. A nanoelectrode was brought within tunneling distance towards a SAM-covered Au sample immersed in 1 M H₂SO₄. A suitable region for the modification was selected and documented.
The etching pits resulting from the formation of the alkanethiolate SAM were later used as landmarks. After moving the probe 1 μm away from the region of interest, the solution in the ECSTM cell was exchanged against 10 μl K2[PtCl4]+1 M H2SO4 using the solution exchange system developed for our setup [42]. Then the probe was repositioned in an ECSTM experiment relative to the landmarks. At the sample potential no Pt deposition occurs at the gold electrode because the SAM passivates the surface. In this situation the probe sample-distance, d, is about 0.5 nm. The feedback regulation of d is switched off for 1 ms and a potential of −391 mV is applied to the tip so that electrodeposition of Pt occurs at the tip. The deposited Pt grows across the tip-sample gap, penetrates into the SAM and contacts the gold electrode (Fig. 7a). When the feedback distance regulation is switched on after 1 ms the produced short-circuit causes the tip to retract and the metal junction is disrupted. At the same time potentials are set to \( E_T = -291 \) mV and \( E_S = -191 \) mV. After parking the tip and a solution exchange against 1 M H2SO4, an ECSTM image proves that a metal dot was created on the SAM-coated gold surface (Fig. 7c). It has a diameter at the base of 53 nm and a height of 18 nm corresponding to a volume of about \( 4 \times 10^4 \) nm3. The size of the cluster is larger than the ones resulting from the jump-to-contact method of Kolb et al. [58]. The potential advantage of our approach compared to other methods for the formation of small Pt particles on surfaces is the fact that the particles are placed on a passivated surface. This should facilitate the investigation of catalytic properties of such particles because the contribution from the much larger substrate surface is suppressed by the inhibiting alkanethiolate film.

### 3.3. Simulation of local concentration and fluxes with the boundary element method

It has already become evident when selecting suitable probe geometries for nanoscale electrochemical experiments (Fig. 1) that a routine to simulate mass transport in such setups is extremely important. We developed an implementation of the boundary element method to simulate steady-state currents in arbitrary geometries [43]. It is based on the transformation of the Laplace equations (2) for the volume diffusion problem

\[
\frac{\partial c(r, t)}{\partial t} = \nabla^2 c(r, t), (r \in V),
\]

where \( \nabla^2 \) is the Laplace operator, \( r \) is a coordinate vector, and \( V \) is a simulation domain, to an integral problem over the domain boundary \( \Omega \) using the Green’s second theorem and the Green’s function \( G \). After discretization using \( N \) boundary elements indexed by \( i \) and \( j \), it gives \( N \) linear algebraic Eq. (3).

\[
\frac{1}{2} c_j = \sum_{i=1}^{N} \left( c_i \int_{\Omega_i} \nabla G_{ij} \vec{n}_j \cdot d\Omega_i - \int_{\Gamma_i} G_{ij} d\Omega_i \right),
\]

\( N \) values of either concentrations \( c_i \) or fluxes \( \frac{\partial c_{ij}}{\partial n_i} \) are given by the boundary conditions. \( G_{ij} \) is the standard Green function for the Laplace equation in 3D [59] calculated on the basis of vectors.
connecting the elements \(i\) and \(j\). The resulting system of \(N\) linear equations is solved for the remaining \(N\) unknown fluxes and concentrations at the boundary of the simulation domain. Summation of the fluxes through the boundary elements that constitute the electrode surfaces provides the probe current. The external formulation of the Laplace problem [43], where the probe and sample are enclosed by the boundary, avoids any assumptions about the extensions of the diffusion layer and leads to a quantitative agreement with experimental data. It is sufficient to develop a mesh on the surface of the probe and the sample. Afterwards the current can be easily calculated for any relative position between them. This constitutes a big advantage over finite difference or finite element schemes which require substantial changes of the numerical procedures when changing form one geometry to another [25,60]. Using this strategy we were able to quantify the influence of the tilt of an UME on image contrast, the dependence of resolution and sensitivity on the thickness of the insulating shielding of SECM probes and the SECM response in constant-distance SECM experiments in the vicinity of a step edge [43]. In addition, experimental data of Ufheil et al. [45] on integrated microheptodes for scanning probe applications could be quantitatively modeled [61]. Different boundary conditions are used to define the particularities of a specific electrochemical system. For the above mentioned application conditions of constant concentrations (diffusion-controlled reaction) and zero fluxes (insulating insert surfaces) were used in normalized coordinates [43]. Meanwhile we expanded the method to treat any flux proportional to the local concentration (first-order reaction at the boundary) [61], any constant concentration, and any constant flux. With this simulation tools a couple of interesting questions in nanoelectrochemistry—also beyond SECM—can be addressed. It has been, for instance, a long standing question how much ECSTM results for metal deposition are influenced by the local decrease of diffusional flux of metal ions to the sample region underneath the ECSTM tip. This problem has been treated by Divisek et al. [62] for the case of high current densities. Recent progress on electrochemical video STM [40] of metal depositions aims to extract macroscopic rate constants for these heterogeneous reactions by appropriate averaging from the observed rates on an atomic scale. This would lead to a new level of microscopic understanding of a large number of technologically important processes [63]. One concern has been the deviation of the local current density \(j\) of metal reduction under the ECSTM tip in comparison to the macroscopic current density.

3.3.1. Setup of simulations

We consider a microscopic arrangement where a heterogeneous reaction \(O + ne^- \rightarrow R\) takes place at the sample and no reaction at the SECM tip. The calculations are made assuming equations and boundary conditions for the reduced form \(c = c_R\) with the diffusion coefficient \(D = D_R\). Triangular elements are used to create a mesh for the sample and the tip. Within every individual element both local flux of \(R\) through the boundary element perpendicular to the boundary element, \(\partial c_i / \partial n_i\), and local concentration, \(c_i\), are assumed to be constant. Fig. 8 shows a mesh generated by a geometry editor and used for the calculation of tip-shielding effects in ECSTM studies of metal deposition. The radius of the tip apex was 1 \(\mu\)m. The working distance was set to 5 nm. This value is large compared to the real situation. However numerical errors are greatly increased if the distance is set smaller than 3 nm because the sample size is then 4 orders of magnitude larger than the smaller critical length. A resting ECSTM tip was

![Image](https://via.placeholder.com/150).

**Fig. 8.** The mesh used for describing the sample and the mesh used to describe the tip. The setup comprises a total of 2833 boundary elements and was created with a geometry editor.
assumed since typical scan ranges in atomically resolved imaged are small in comparison to the radius of the tip apex.

Fig. 9a shows the local current densities when no tip is present and the integrated current density is \( \langle j \rangle = 8.0 \, \text{µA cm}^{-2} \). There is a smooth variation of \( j \) over the sample due to an enhanced mass transport at the edges of the sample. Fig. 9b shows the local current densities if the ECSTM tip is located in a distance of 5 nm over the center of the sample. The local current density is decreased in the center of the sample. The difference of local current densities resulting from the presence of the tip is plotted in Fig. 9c and scaled to the average macroscopic current density. It is evident that at the average current density of 8.0 µA cm\(^{-2}\), the deviation of the reaction current density under the tip does not exceed 15% of the average value.
Similar calculations were performed for current densities of 1.1–27.1 \( \mu \text{A cm}^{-2} \). The relative differences of local current densities are given in Fig. 10 for cross-sections through the lateral position of the tip center. Within the considered range of \( \langle j \rangle \) the local variations of \( j(x,y) \) under the tip change from insignificant values of about 1% for \( \langle j \rangle = 1.1 \mu \text{A cm}^{-2} \) to substantial differences of 70% at \( \langle j \rangle = 27.1 \mu \text{A cm}^{-2} \). Current densities used in ECSTM imaging of Cu depositions are in the range of 1–10 \( \mu \text{A cm}^{-2} \) [64]. At these current densities the deviation of \( j(x,y) \) under the tip compared to \( \langle j \rangle \) is below 15%. Therefore, kinetic data extrapolated from the microscopic observation should not be significantly influenced by diffusional shielding of the tip.

4. Conclusion

Electrodes having an active electrode surface with an effective radius of about 10 nm have been prepared. They can be effectively used in both ECSTM and SECM experiments in a customized scanning probe instrument. Their shape corresponds to that of shallow cones for which a theoretical description was obtained by the BEM. Their size can be conveniently tuned in the range of 10–400 nm effective radius. Combined ECSTM and SECM imaging of patterned self-assembled monolayers of alkanethiols on gold was demonstrated. Reactivity differences of damaged monolayer areas of \( 100 \times 100 \text{nm}^2 \) with a mutual distance of 750 nm could clearly be detected and resolved. This demonstrated clear perspectives for reactivity images and analysis in the nanometer size regime.

The setup is also useful for the local electrochemical surface modification in the nanometer scale. This is demonstrated by an electrolytic Pt deposition on an alkanethiolate SAM-covered gold surface using a grow-to-contact approach. A nanodot with 53 nm diameter and 18 nm height was formed and consisted of a catalytically active metal placed onto a passivated support surface. Alkanethiolate SAMs were also locally removed by an electrochemical desorption procedure. In comparison to a similar procedure in the micrometer range, desorption times of 1 ms and lower ac voltages had to be used. The ability to perform local reactivity imaging simultaneously with ECSTM imaging as well as to induce local electrochemical surface modification in the same setup opens up new perspectives for the investigation of heterogeneous reactions in electrocatalysis at metal clusters and in corrosion processes in a new size regime. Further expansion of the experimental strategies mainly depends on the preparation of more robust nanoelectrodes that are less susceptible to changes in the active electrode area.

Currently, the stability of the used probe electrodes is limited. While a stable electrode response was observed in a number of cases, it may change rather rapidly without external disturbance, possibly as a consequence of alterations of the thin electropolymerized film close to the active electrode area. This constitutes a significant experimental problem.

The quantitative understanding of nanoelectrochemical experiments requires the simulation of the diffusion fluxes in microscopic domains. Due to the complicated geometrical situation finite differences and finite elements simulation approaches are not very well suited as the required simplifying assumptions about the system geometry are particularly problematic in nanoelectrochemical systems and in systems that lack an axial symmetry. The developed BEM simulation tool allows the theoretical description of mass transport in micrometer and nanometer-sized cell assemblies independently of particular geometries. Here it could be shown that the local current density underneath a tip in ECSTM investigations of copper deposition does not deviate more than 15% if the integral current density remains below 8 \( \mu \text{A cm}^{-2} \) and the deviation is around 1% at current densities of 1.1 \( \mu \text{A cm}^{-2} \). These results support attempts to derive macroscopic kinetic expressions by averaging over local reaction rates measured at different surface sites on an atomic level.

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