

A New Approach to Micropatterning: Application of Potential-Assisted Ion Transfer at the Liquid–Liquid Interface for the Local Metal Deposition

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The formation of controllable micro and nanometer size patterns at interfaces is currently a significant area of research.¹ Although lithography² and scanning probe microscopy³ have often been applied, electrochemical scanning probe methods offer an alternative approach for the deposition of micrometer and nanometer structures.⁴

We report here on a new approach to deposit micropatterns by the scanning electrochemical microscope (SECM) which is based on ion transfer across a micro interface between two immiscible electrolyte solutions (micro-ITIES). The SECM is a scanning probe microscopy technique, which is capable of generating a flux of electroactive species at a tip that is held close to an interface.⁵ The tip–interface distance is usually monitored by the Faradaic current at the tip, which is sensitive to the interaction between the species and the interface. Micro to nanometer structures have been deposited by the SECM⁶ due to the fact that electron transfer is localized on the surface beneath the tip.

The concept of micro-ITIES has been introduced by Girault⁷ and recently applied with the SECM for imaging and studying charge transfer locally at interfaces.^{8–12} The essence of the method is to replace a solid microelectrode with a micropipet filled with a liquid phase that is polarized vs an outer phase. The controlled polarization drives the transfer of ions across the liquid/liquid interface. The scanning ion conductance microscopy developed by Hansma¹³ and applied^{14,15} for the deposition of metals has some similarity, however, the concept presented here of creating a controllable flux of ions from a micropipet across an ITIES has never been used for depositing small patterns. The setup is shown schematically in Figure 1.

The approach is based on the transfer of silver ions, across a liquid/liquid interface at the tip of a micropipet that is dipped in an outer organic solution of nitrobenzene (NB), consisting of the electrolyte tetrabutylammonium tetrakis[4-chlorophenyl]borate (TBATPBCl). Figure 2 shows the cyclic voltammetry (CV) of a micropipet carried out as previously described.¹⁶ To prevent from the inner aqueous solution to form a thin layer on the outer wall, the latter was silanized.¹¹ The potential window through which the species are transferred across the liquid/liquid interface depends on the difference between the Gibbs free energy for ion transfer of the species in both phases. Therefore, the organic solvent and the electrolytes must be carefully optimized. We are aware of only a few studies on the potential assisted transfer of silver ions.^{17,18}

To reduce the Gibbs free energy of Ag(I) transfer and facilitate its transfer dibenzo-24-crown-8 (DB24C8) was added to the organic phase. The decision which ligand to use is a compromise between the need for strong and fast complexation to assist the egress of Ag(I) while maintaining the ability to reduce the Ag(I) complex under moderate potentials. From the sigmoid shape of the anodic

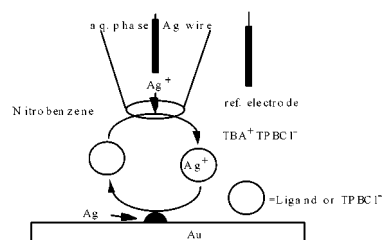


Figure 1. Schematic representation of the concept for patterning through the potential assisted ion transfer at the liquid/liquid interface.

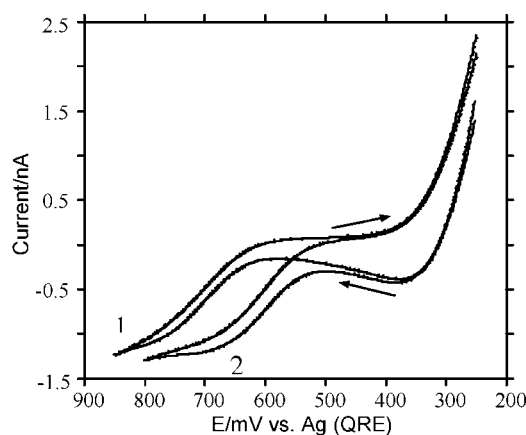


Figure 2. CV of a 1.5 μm radius micropipet filled with 5 mM Ag_2SO_4 (pH 5.0) in NB consisting of 10 mM TBATPBCl, before (1) and after (2) adding 20 mM DB24C8. The scan rate was 10 $\text{mV}\cdot\text{s}^{-1}$.

wave it is evident that silver ions are transferred from the inner phase outside. The transfer is controlled by the spherical diffusion of the ligand, which results in a steady-state current. The steady-state current in the reverse scan is due to the spherical diffusion of Ag(I) from the organic phase back to the micropipet.¹⁹ The negative potential range in the CV is limited by the ingress of the cation, TBA^+ .

We have further exploited the potential controlled flux of Ag^+ as a means of forming micropatterns of Ag on Au using the SECM. One essential feature of all SPM techniques is the ability to control the tip–surface distance. Usually this is accomplished in the SECM by monitoring the Faradaic current of the tip. The current of the micropipet originates from the egress of Ag^+ . This flux cannot provide the mechanism of controlling the microelectrode–surface distance unless it depends on diffusion of species in the organic phase. However, since the transfer of Ag^+ is assisted by either the anion of the electrolyte or the ligand in the organic phase, maintaining their concentration comparable with that of Ag^+ (in the micropipet) makes the Faradaic current be dependent on their diffusion (Figure 1).

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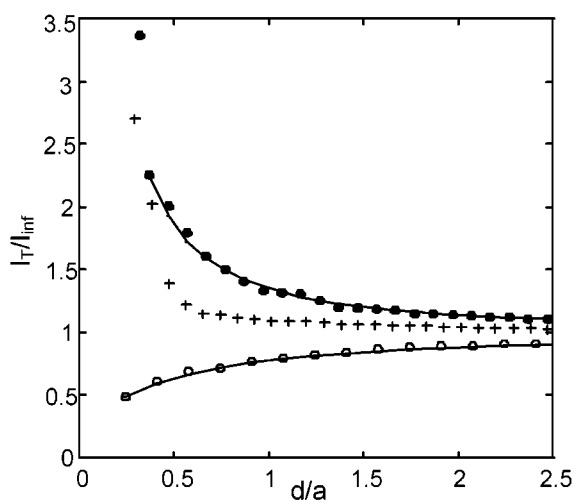


Figure 3. Normalized feedback curves recorded with a silanized $2.5 \mu\text{m}$ radius micropipet ($E_T = 0.9 \text{ V}$) filled with $5 \text{ mM Ag}_2\text{SO}_4$ (pH 5.0) approaching ($1 \mu\text{m}\cdot\text{s}^{-1}$) a gold substrate in a NB solution of 2 mM TBATPBCl and 20 mM DB24C8 . The potential of the surface was (○) 0.6 V , (+) 0 V or unbiased (●) vs an Ag wire in the organic phase. Solid lines represent the theoretical negative and positive feedback currents.

Figure 3 shows the steady-state feedback current recorded while approaching an Au substrate held at 0.6 V , a potential that prevents Ag(I) reduction. It can be seen that the current of the microelectrode matches well the theoretical negative feedback current calculated for tips with a thin insulating sheath (a 1.1 ratio of insulator to metal radius was used).¹⁰ Figure 3 shows also the feedback current acquired above a gold substrate held at 0 V . An increase of the steady-state current at the micropipet is observed as the tip approaches the surface. The positive feedback current is the best indication that silver ions are reduced on the gold surface, regenerating the free ligand, which plays a key role in establishing the positive feedback current. Interestingly, the current increases also while approaching a gold surface in the absence of the crown ether. This must be due to the TPBCl^- in the organic phase that stabilizes the silver ions. The approaching curve recorded above an unbiased gold surface fits perfectly the theoretical curve for a conducting substrate¹⁰ and is driven²⁰ by the difference in the Nernst potential in the volume between the micropipet and the surface and the rest of the solution. We believe that deposition occurs on an unbiased surface due to the relative negative OCP (-0.16 V vs Ag wire) that is sufficient to drive the deposition of small amounts of silver.

The positive feedback current as well as the dramatic increase of the current, which was observed shortly after the micropipet was brought in close proximity to the substrate (Figure 3), indicates the relatively fast growth of the deposit beneath the micropipet. Indeed, reproducible and stable patterns of silver were easily formed locally. Figure 4 shows a SEM image of a gold surface on which silver dots were deposited as a result of holding the micropipet above an unbiased gold surface for only a few seconds. The height of the silver deposits reaches ca. $0.3 \mu\text{m}$ (measured by profilometry). It is expected that a high aspect ratio of the structures can be achieved if the pipet is continuously withdrawn from the deposit. The width of the spots is affected by the micropipet size, the surface–tip distance, the concentration of electrolyte and the time

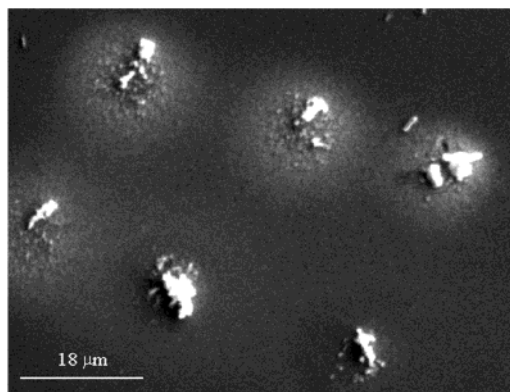


Figure 4. SEM image of a gold surface with deposited silver dots. Microstructures were deposited under the same conditions as those in Figure 3 employing a nonbiased gold substrate.

that the micropipet is left above the surface. EDX analysis proved unambiguously that the patterns are made of silver.

In conclusion, we have demonstrated that the combination of potential assisted ion transfer across liquid/liquid interfaces and the SECM can be used for micropatterning. This approach is very versatile and will enable us to implement it in other systems, for example, conducting polymers, providing that the system is appropriately configured. Moreover, the construction of micropipets with holes of the order of tens of nanometers is simpler than the fabrication of nanoelectrodes. Finally, combining this approach with either the shear force mode of the SECM^{21,22} or AFM will allow the formation of nanostructures with very high lateral resolution.

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