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**Novel Focused Ion Beam-Milled Probes for Combined
Scanning Electrochemical Microscopy – Atomic Force
Microscopy**

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Novel Focused Ion Beam-Milled Probes for Combined Scanning Electrochemical Microscopy – Atomic Force Microscopy

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ABSTRACT

A novel approach to the fabrication of dual function probes for combined scanning electrochemical microscopy – atomic force microscopy (SECM-AFM) is described. Silicon nitride AFM probes were machined using a focused ion beam (FIB) procedure to produce a 100 nm aperture through the apex of the tip. Subsequent filling of the aperture with platinum using beam-assisted metal deposition yielded a platinum nano-electrode at the tip apex. Insulation of the reverse side of the cantilever was achieved using beam-assisted tetraethyl orthosilicate (TEOS) deposition.

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Approved on behalf of NPLML by Dr M G Cain, Knowledge Leader,
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GLOSSARY/ABBREVIATIONS

AFM	Atomic force microscopy
CV	Cyclic voltammogram
EFM	Electric force microscopy
FIB	Focused ion beam
SECM	Scanning electrochemical microscopy
SEM	Scanning electron microscopy
SiN	Silicon nitride (probe)
TEOS	Tetraethyl orthosilicate

1 INTRODUCTION

Since its inception in the late eighties, scanning electrochemical microscopy (SECM) has matured into one of the most versatile and informative techniques used in electrochemical science today.^{1,2} The ability to map interfacial processes with spatial resolution and to monitor local surface reaction kinetics has given rise to a breadth of applications, including studies into biological processes,³⁻⁶ corrosion^{7,8} and dissolution^{9,10} phenomena, and electrocatalyst activity.^{11,12} SECM typically involves immersing the sample of interest into an electrolyte solution and scanning an electrochemical probe at a fixed height (often at a distance of the order of microns) above the surface. In the conventional amperometric mode the solution contains a redox mediator, which is electrolysed at the tip of the probe and the measured Faradaic current is sensitive to the local environment. In the vicinity of inert surface features, the hindered diffusion of fresh mediator limits the current (negative feedback), whereas conducting or catalytically active regions can regenerate the original oxidation state of the mediator, leading to an augmented current response (positive feedback). It is this unique chemical sensitivity that lends SECM its remarkable efficacy.

The spatial resolution of SECM is governed primarily by the dimensions of the sensing probe. Typically, ultramicroelectrodes with diameters in the 1 μm – 25 μm range are employed, although some conventional SECM measurements have been demonstrated using submicron-sized electrodes.¹³⁻¹⁵ The major challenge in achieving nanometre scale resolution lies not simply in the fabrication of the necessary nano-sized probes, but also in addressing the sensitivity of the measured current to tip-surface separation. Since the current response is a convolution of both surface topography and activity, constant height scanning measurements are complicated by the problem of a constantly changing tip-substrate distance. This severely limits the application of high resolution SECM to only very flat samples where the influence of topography can either be neglected or approximately corrected for by the addition of a second redox mediator. Even then, the likelihood of tip-surface impact is increased dramatically by the short working distances required for nanoscale measurements. The most effective means of circumventing the above difficulties is for scanning to be carried out at constant tip-surface separation to allow surface activity to be measured independently of topography.

A number of elegant approaches have been developed in which the electrochemical probe is able to respond in real time to follow the surface topography. The shear force feedback method is one such approach, which involves laterally oscillating the probe tip and monitoring the damping experienced at close proximity to the surface.¹⁶⁻¹⁸ A number of modes and applications of this technique to nanoscale SECM have been demonstrated.¹⁹⁻²¹ Another attractive approach, which has received attention from a number of research groups, is to combine SECM with atomic force microscopy (AFM).²² This involves the development of dual function SECM-AFM probes, which respond to surface topography using the conventional AFM feedback mechanism, whilst allowing electrochemical measurements on an integrated electrode. SECM-AFM probe fabrication strategies are varied, and range from the modification of existing AFM tips to batch fabrication from wafer level.²³⁻³² One inventive approach, pioneered by Kranz *et al.*, involves using microfabrication techniques to produce an AFM probe with an integrated ring electrode.^{27,28} The electrode is recessed at a specified distance from the tip to allow simultaneous acquisition of topographical and electrochemical information. Whilst the topographical resolution is akin to that of regular AFM, the electrode has dimensions in the order of microns, which limits the spatial resolution of the electrochemical measurements. An effective approach to gaining improved

electrochemical resolution was demonstrated by Macpherson and co-workers.²⁴ A carbon nanotube is attached to the apex of an AFM tip and used as a template for metal sputtering. Subsequent insulation and focussed ion beam milling on the nanowire probes yields a high aspect ratio tip with an addressable nanodisk electrode at the end. For this type of probe the tip-substrate separation can be controlled for the electrochemical measurements using “lift-mode” in which the tip first traces the topography and subsequently re-scans each line at a fixed distance above the surface. A drawback of the many fabrication procedures described in the literature is their complexity, which has limited their use to specialist research groups and prevented widespread commercial availability.

One of the most challenging aspects of probe design is the problem of insulation. The electroactive region of the tip must be well defined and the remainder of the probe sufficiently insulated so as to avoid Faradaic processes elsewhere. Thus the electrochemical measurements are localised to a known point of interest. A common strategy is to begin with a metal coated probe and add conformal layers of insulation on top. Coating materials that have been used include Parylene C, silicon nitride, electrophoretic paint and poly(oxyphenylene). The problem with this “building up” strategy is that in order to obtain sufficient levels of insulation, the coating thickness required is generally of the order of hundreds of nanometres which, except in the more elaborate designs,²⁸ can compromise the topographical resolution.

In this work we explore an alternative approach to SECM-AFM probe fabrication. Instead of building outwards from a standard AFM probe, we mill *inwards* using focused ion beam (FIB) technology to integrate a working electrode connected through the interior of the pyramidal tip. This way the exposed metal region is a well-defined point at the apex of the tip with nanoscale dimensions, and the remainder of the imaging side of the probe is insulated by the silicon nitride base. A similar approach was adopted by Menozzi and co-workers³³ for the fabrication of probes for electric force microscopy (EFM). The only additional requirement for the SECM-AFM application is the necessity to insulate the electrical connection pathway on the rear side of the cantilever (see Figure 1). Since the cantilever itself does not affect the imaging resolution, the thickness of insulation added to this part of the probe is not an issue, and so localised insulator deposition can be used. The advantage of this approach as compared to the nanotube method of Macpherson *et al.*²⁴ is the improvement in topographical imaging resolution without compromising the electrochemical resolution.

This report details the fabrication of such probes and explores their potential application to SECM-AFM imaging.

2 EXPERIMENTAL

2.1 MATERIALS

All chemicals and solvents used were of the highest commercially available purity and were used as-received. Hexamine ruthenium (III) chloride was purchased from Acros Organics and hexachloroplatinic acid from Aldrich. Silver conducting paint was purchased from RS Components. Cathodic electrophoretic paint (Clearclad HSR) was kindly donated by LVH Coatings, Birmingham, UK. Water with a resistivity of not less than 15 MΩ cm was taken from an Elga Purelab water purification system. A variety of silicon nitride probes were used in the development of SECM-AFM probes, including Veeco NP, SNL and OTR, Budget

Sensors TAP300Al and Nanoworld PNP-TR (purchased through Windsor Scientific, Slough, UK).

2.2 INSTRUMENTATION

Electrochemical experiments were undertaken using a CH Instruments (Austin, Tx, USA) model 760C bipotentiostat equipped with a CHI200 picoamp booster. The picoamp booster was attached to a purpose built Faraday cage that was fitted over the AFM scanner and head. Probe electrochemistry was tested with the aid of a Veeco (Santa Barbara, CA, USA) MultiMode AFM with a Nanoscope IIIa controller, supported on an anti-vibration table (TMC, Peabody, MA, USA). SECM-AFM probes were mounted into a Veeco fluid cell, modified to allow electrical connection to the probe via the spring loaded metal clasp. A small amount of conducting silver paint was used to ensure good electrical connection. Bulk insulation of the probe and clasp was achieved using a combination of nail varnish and superglue (Loctite 407, Farnell Electronic Components Ltd),²⁵ which was left to cure at room temperature for several hours after application. A silver wire was inserted into one of the fluid inputs to the cell and was used as a reference/counter electrode. Electron micrographs were acquired using a Zeiss Supra 40 SEM. Focused ion beam (FIB) milling was achieved using an FEI Nova Nanolab 600 dual beam FIB.

2.3 PROBE DEVELOPMENT

2.3.1 Commercial Probe Types

A range of commercial silicon nitride (“SiN”) probes were tested for suitability for the FIB machining procedure. Silicon nitride was chosen as a probe material since it is intrinsically electrically insulating, removing any requirement to add additional insulation layers to the tip of the probe. By contrast, standard silicon probes are typically doped and are therefore semiconducting. It was noted that the Veeco SiN probes in fact comprised silicon nitride *deposited onto* a silicon base. This is an important issue when using FIB, since if the surface is milled significantly, semiconducting silicon can be exposed, which may compromise the probe insulation. A number of other criteria were also considered.

Firstly, the nature of the pyramidal tip is especially important. Whilst some modern commercial SiN probes consist of a solid pyramidal tip attached to a cantilever (Veeco NP and SNL), the majority of older probes (TAP300Al, OTR and PNP-TR) have a hollow pyramidal tip, i.e. there is a cavity on the reverse side (see Figure 2a and b). Milling an aperture through the tip using FIB requires the milled material to be released out from the hole, such that milling through large volumes of material becomes problematic. Thus, the less material that needs to be milled through, the more narrow the aperture can be. Consequently it was considered advantageous to use the hollow type probes. Furthermore, with the solid-tip probes it is particularly difficult to ascertain the correct position on the rear side of the cantilever to allow the milled aperture to coincide with the apex of the tip. This is not a problem with the hollow tips as the apex can easily be identified from the rear (see Figure 2c). There are methods to circumvent the problems associated with milling solid tips and these will be discussed further in Section 2.3.2.

Tip shape is a feature that should be considered, but does not influence the FIB procedure. It was noted that, in contrast to the vast majority of probe types, which consist of a single pointed pyramidal tip, the hollow TAP300Al probes comprise double pointed tips (see Figure

2d). Providing the second tip does not interfere with imaging, this issue was considered not to be significant.

Finally, the probe body shape is an important issue with regards making the electrical connection to the deposited nanoelectrode. A conducting platinum line is deposited along the reverse side of the cantilever between the tip and the probe body, and this is continued up along the body of the probe so that a wire can be connected. The nature of the edge of the probe body at the point where it meets the cantilever has a significant impact on how difficult and time consuming the platinum line deposition is. There are two basic shapes, either a 'sloping' edge (TAP300Al, NP, SNL) or a single step edge (OTR and PNP-TR), and these are depicted in Figures 2e, f and g. Platinum deposition on the sloping edge (Figure 2f) is challenging since not only is the length of the sloping edge quite long (of the order of mm), on the local scale the surface is in fact ridged, which adds the requirement for frequently changing the angle at which the sample is orientated in the FIB. On the other hand, the single step (Figure 2g), is relatively short and only has to be held in two orientations, making platinum deposition much simpler and less time and resource intensive.

Taking into account all of the above, the PNP-TR probes were considered to be the most appropriate for this application.

2.3.2 Focused Ion Beam (FIB) Milling

The cantilevers were placed tip down on a simple silicon substrate. A thin strip cut from a carbon adhesive disc (Agar Scientific, UK) was used both to hold the cantilevers down and to raise the cantilever body above the substrate so that the tip was clear of the substrate. Then, imaging the back of the cantilever, the tip was located and a 30 pA ion beam was used to mill a hole through the tip. Typically this was achieved in under a minute. With the hollow type tips, alignment was simple as the edges of the pyramidal tip provided a set of alignment marks running to the apex of the tip (see Figure 2c). With the tip located just above the silicon substrate it was also very simple to check if the milled hole had fully penetrated the tip, as a small milled hole would also appear in the silicon substrate below. Once a time had been established to mill one hole, it was found to be repeatable from tip to tip.

As discussed in section 2.3.1, FIB aperture milling is much simpler with the hollow-type probes. Figure 3a depicts the topside of such a probe with a *ca.* 150 nm diameter aperture successfully milled through the apex. The aperture diameter depends on various parameters, including the beam current, but apertures as narrow as 100 nm were possible with the lowest currents. The possibility of milling apertures in the solid tips was also investigated. This involved firstly cutting away a circular disc of material from the topside of the cantilever using FIB (Figure 3b). This served not only to aid the subsequent aperture milling by reducing the volume of material required to mill through, but also to expose a shadow of the tip position on the topside of the cantilever in order to facilitate positioning of the aperture when imaged at high accelerating voltages. By gradually removing discs of material and milling deeper into the rear side of the cantilever, the tip could essentially be hollowed out before milling the aperture. Figures 3c and d depict the resulting aperture from the reverse and tip sides of the cantilever. Note that the size of the aperture in the solid tip is somewhat larger than that achieved with the hollow tip for the reasons discussed above. One additional problem observed with the solid tips was the variation in geometry of the pyramidal tip. Some of the tips were not quite perpendicular to the cantilever, and so when milled the hole did not emerge at the very apex of the tip (see Figure 3d).

2.3.3 Platinum Deposition

Platinum deposition was required both to fill the aperture in order to yield a nanoelectrode at the tip apex and in order to provide an isolable conducting path to the point of connection on the probe body. Two approaches to platinum deposition were investigated.

The first approach was electrochemical deposition, achieved by immersing the probes into a platinum salt solution and applying a cathodic bias to the probe. The probe was held in place in the solution by clamping it in a fine point crocodile clip (RS components) and mounting this onto a micropositioner (422 Series, Newport, UK). This allowed the contact with the solution to be carefully manipulated. A solution of 0.5 mM hexachloroplatinic acid (H_2PtCl_6) in 0.1 M sulphuric acid was used for the electrochemical deposition, with a silver wire quasi-reference electrode. A range of deposition potentials and times were tested and the tips subsequently analysed using SEM. FIB was used to cut away a cross section through the tip in order to determine whether the aperture was successfully filled. Figures 4a and b demonstrate results obtained using two extreme deposition potentials of 0.1 V and -0.4 V respectively, each for a duration of 1 hr. In the case of the mild deposition potential of 0.1 V, there is very little deposition observed, and the aperture is clearly unfilled. With the more cathodic bias of -0.4 V, significant platinum deposition is visible around the outside of the tip and cantilever, but again no platinum was present in the aperture. Furthermore, the platinum does not appear to be well adhered to the cantilever surface. Since no platinum could be deposited within the aperture under any of the conditions tested, and due to the rather uncontrollable nature of the platinum growth, this method of deposition was deemed unsuitable for this purpose.

The second approach was based on a procedure demonstrated by Menozzi and co-workers³³ who used beam-assisted platinum deposition to fabricate EFM probes. Essentially this method is ion beam assisted chemical vapour deposition. An organometallic precursor (methylcyclopentadienyl-tri-methyl-platinum) is used to provide the platinum material and is introduced into the FIB chamber as a gas via a needle positioned 50 μm above the sample surface. This gas is then dissociated by the ion beam, leaving behind a platinum rich deposition that also contains some gallium from the ion beam, and carbon from the precursor. Using this technique, it was possible to fill the aperture with platinum initially from the rear side of the cantilever and completing the deposition from the tip side. The result can be seen in Figures 4c and d, which depict the filled tip from both sides of the cantilever. Connection lines were also deposited along the cantilever as depicted in Figure 4e. These connections were extended up the edge of the probe and onto the top of the main body, terminating with a large (*ca.* 200 square micron) connection pad (see Figure 4f and schematically in Figure 4g). Note that some commercial probes have multiple cantilevers attached as seen in Figure 4f, but the unmodified cantilevers were typically removed at the end of the probe modification process.

2.3.4 Probe Insulation

Insulation of the exposed platinum connection lines was necessary in order to ensure that all electrochemical currents originate only from the nanoelectrode positioned at the apex of the pyramidal tip. In a similar fashion to above, the connection lines and exposed platinum on the rear side of the cantilever was covered using a beam-assisted procedure to locally deposit a layer of silicon oxide. For this to be successful, it was first necessary to isolate these connection lines from the gold layer that covers the cantilever and probe body (this layer is

typically added by the manufacturer to improve reflectivity). This was achieved by using the FIB to mill away the gold from the surface at all regions where it was connected to the deposited platinum in order to isolate the conducting pathway (see Figure 5).

The insulating layer was deposited using the same method as the platinum. In this case the precursor consisted of two-parts, TEOS (tetraethylorthosilicate) and water vapour. When the TEOS chemical is dissociated by the ion beam two products are formed, ethanol and silicon oxide. The ethanol was pumped away by the vacuum system and silicon oxide deposited. The deposit does contain some gallium from the beam and so is not as insulating as pure silica, but was deemed sufficient. The thin lines of platinum were covered with wider strips of insulator, and using the SEM it was possible to see how complete the coverage was. The deposited material is inherently low contrast in the SEM, whereas the platinum is very high contrast. Using a moderate accelerating voltage (10 kV) the platinum lines were imaged as they were covered. When they no longer showed any contrast, and the region appeared quite dark, the insulator deposition was expected to be of the order of several hundred nm thick.

3 RESULTS AND DISCUSSION

The SECM-AFM probes were assessed electrochemically by sealing into a modified AFM fluid cell and immersion into a 1 mM solution of $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ containing 0.1 M KNO_3 . For determination of the exposed electrochemical area and the performance of the insulation, the probe was lowered into a droplet of solution such that just the cantilever was exposed. This was achieved by monitoring the cantilever using the video camera of the AFM. Doing this allowed solely the electrochemistry of the cantilever to be assessed without any contributions from the probe body. A typical CV is depicted in Figure 6 wherein an inflexion in the current occurs at a potential of approximately -0.35 V vs. Ag , which can be attributed to the reduction of $\text{Ru}(\text{NH}_3)_6^{3+}$ to $\text{Ru}(\text{NH}_3)_6^{2+}$. There is clearly an additional process beginning to take place at more cathodic potentials, which may be due to the presence of oxygen in the solution. On the reverse scan there is a discernable peak due the re-oxidation of $\text{Ru}(\text{NH}_3)_6^{2+}$ indicating that there is a transient element to the CV at this scan rate (as opposed to a pure steady state CV in which a flat plateau is expected). Most importantly, the Faradaic current measured is close to 60 nA. If we treat the electrochemically exposed region of the probe as a disc geometry, the relationship between the diffusion controlled limiting current (i_{lim}) and the disc radius (r), assuming convergent diffusion, is:³⁴

$$i_{\text{lim}} = 4FrDc \quad (1)$$

where F is Faraday's constant (96485 C mol^{-1}), D is the diffusion coefficient of the redox active species (for $\text{Ru}(\text{NH}_3)_6^{3+}$ we used a value of $8.9 \times 10^{-6}\text{ cm}^2\text{ s}^{-1}$),³⁵ and c is its concentration. Based on this, 60 nA corresponds to a disc radius of *ca.* 170 μm . Alternatively we can treat the electrode as a hemisphere, in which case the limiting current is given by:³⁴

$$i_{\text{lim}} = 2\pi FrDc \quad (2)$$

From this we calculate a hemisphere radius of *ca.* 110 μm .

Based on SEM inspection of the probe (Figure 4c), we would expect this radius to be in the order of hundreds of nm, indicating that there is clearly a current leakage problem. This is consistent with either insufficient/incomplete TEOS insulation, or poor isolation between the

deposited Pt connection lines and the gold layer on the surface of the cantilever. Given that a disc with a radius of the order of one hundred microns could easily cover the whole cantilever, it is most likely that poor isolation is the issue and that a connection still exists between the deposited platinum and the gold coating on the cantilever.

There are a number of potential solutions to the connection isolation problem. Since the main issue results from the 50 nm conducting gold coating deposited on the rear of the cantilever by the manufacturer, removal of this layer completely could help significantly. The difficulty with this is that it would leave behind a highly insulating SiN cantilever that would be very difficult to manipulate in the SEM/FIB due to electrical charging and subsequent sample movement. One option would be to re-deposit a thinner layer of gold (~10 nm) on the cantilever, enough to aid the FIB procedures, but without providing a robust electrical connection to the platinum connection lines. Alternatively, it may be possible to selectively etch the gold from the cantilever, to leave behind the 5/10 nm chromium adhesive under-layer. A more challenging solution may be to fully remove the conducting coating from the cantilever and deposit the platinum connection lines, only starting from the rigid base and gradually working along the cantilever. This way, any charging problems will be dissipated by platinum connection deposited. Electrochemical deposition of an insulating material could also be used cover all exposed conducting regions, but this would require an additional FIB step to remove insulator from the tip apex to re-expose the electrode. The above potential solutions will be the subject of future investigations.

4 CONCLUSIONS AND OUTLOOK

In this report we have detailed the progress to date in the fabrication of novel probes for SECM-AFM. Whilst in theory this approach has the potential to allow significant improvement in the resolution of the technique, there remain obstacles that need to be addressed. This work highlights the potential pitfalls in such probe development and indicates the important factors that need to be considered, such as probe types and deposition methods.

The development of SECM-AFM probes continues to be a very challenging problem, and as such the use of this technique is not widespread. However, with improvements to resolution, ease of fabrication and the eventual commercial availability of such probes, the full potential of this powerful approach may be realised, and will ultimately serve to improve our understanding of electrochemistry at the nanoscale.

5 ACKNOWLEDGEMENTS

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6 FIGURES

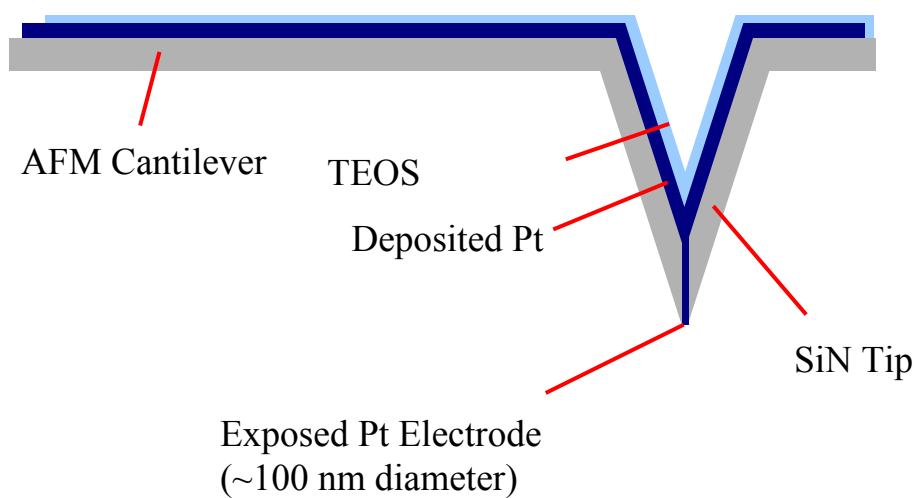
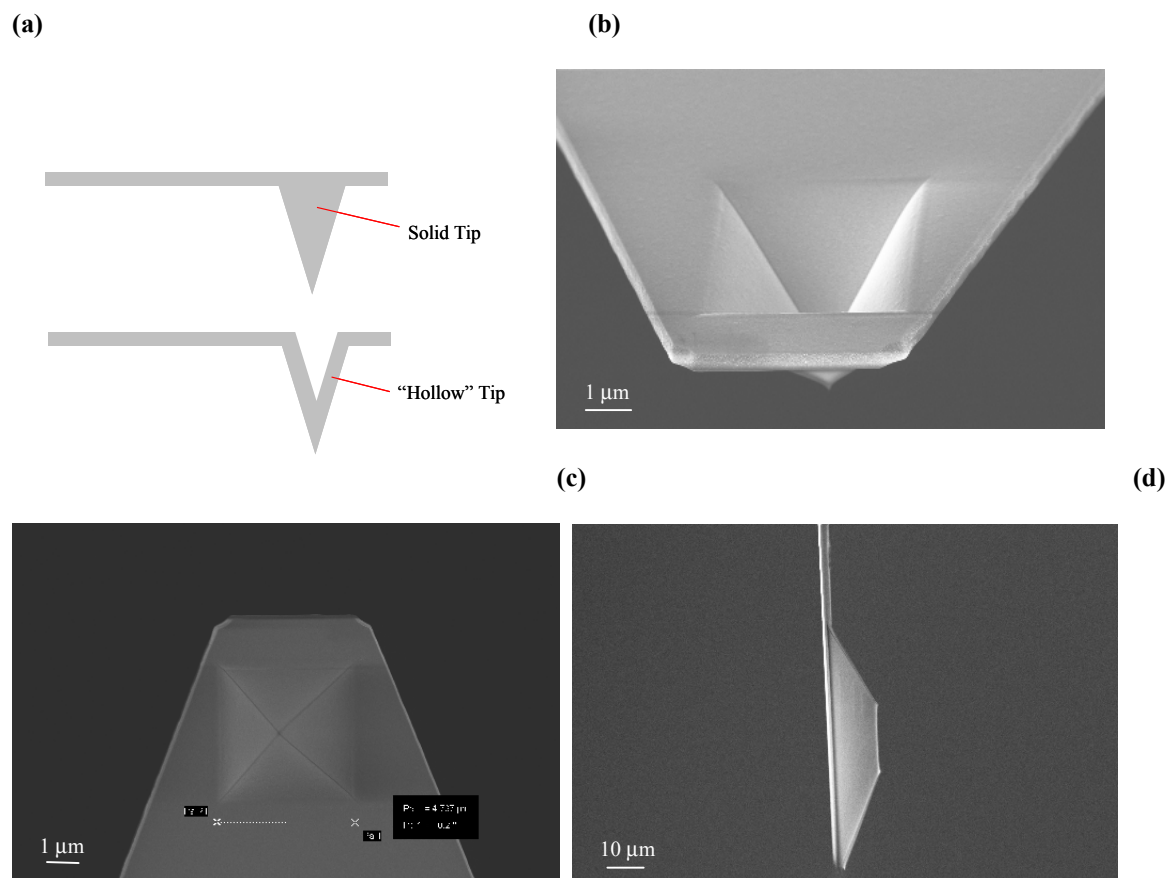


Figure 1 Schematic depiction of SECM-AFM probe design



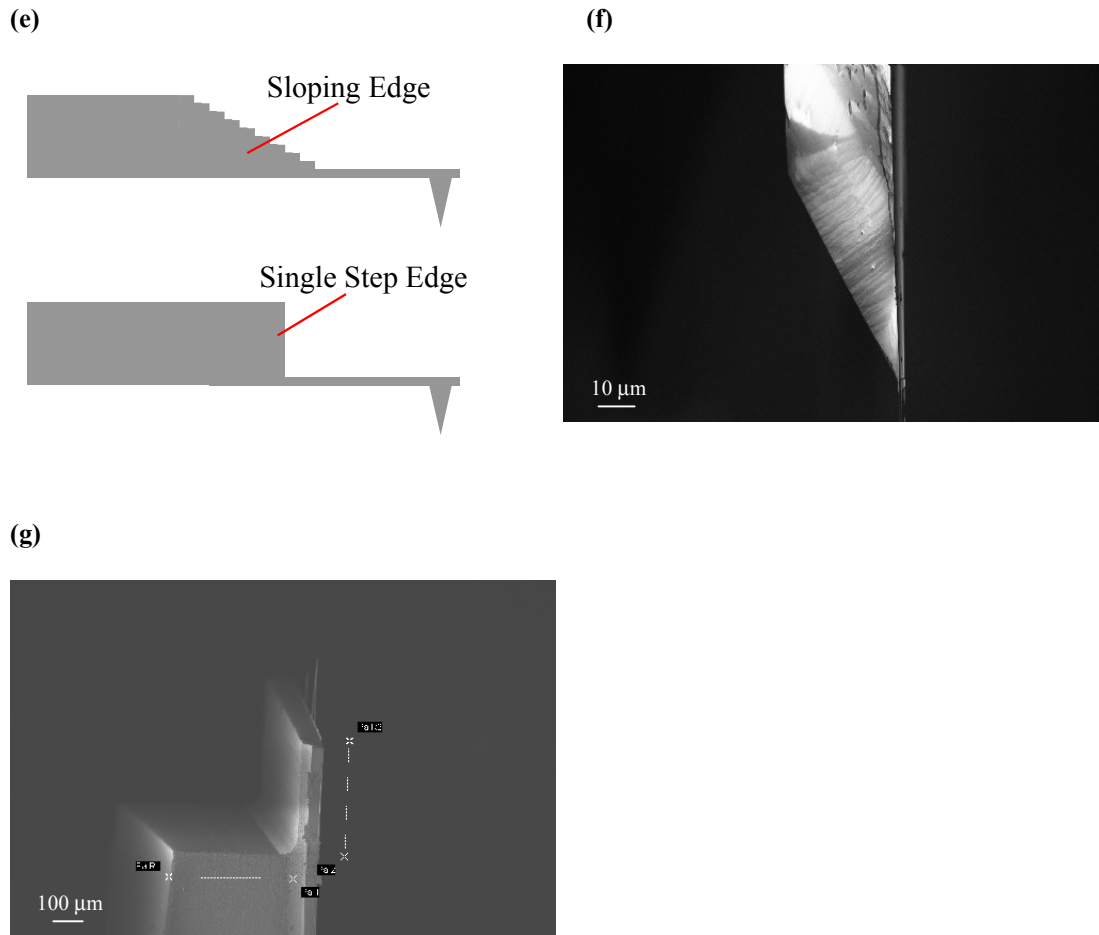
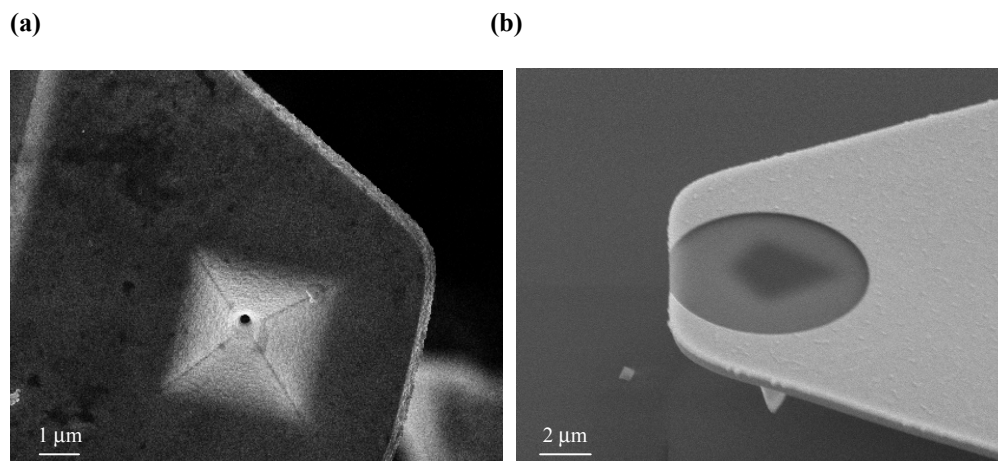


Figure 2 Important features of commercial AFM probes. (a) Schematic depiction of solid and 'hollow' tips in cross section. SEM images of (b) the hollow side of a PNP-TR cantilever, (c) the reverse side of a PNP-TR cantilever clearly showing the position of the pyramidal apex, (d) a double tipped TAP300Al, (e) schematic depiction of sloping and step edges, (f) sloping body edge of a TAP300Al probe and (g) single step edge of a PNP-TR probe.



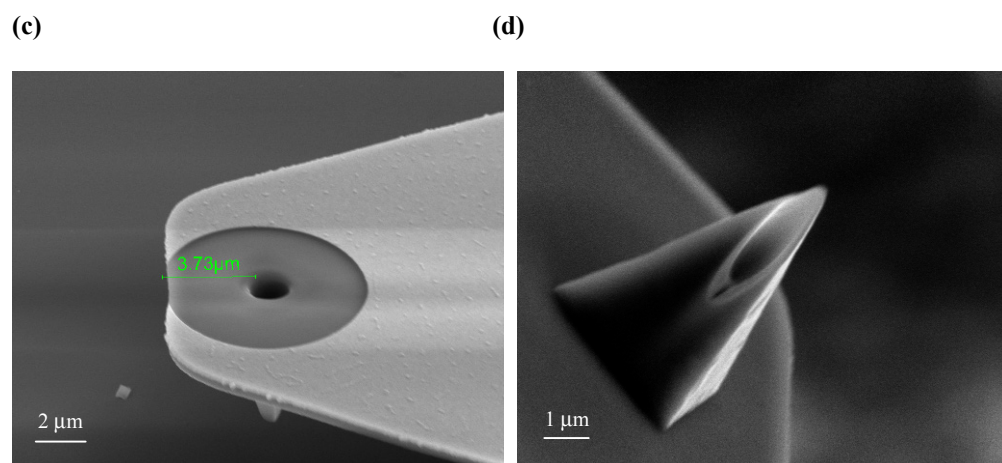
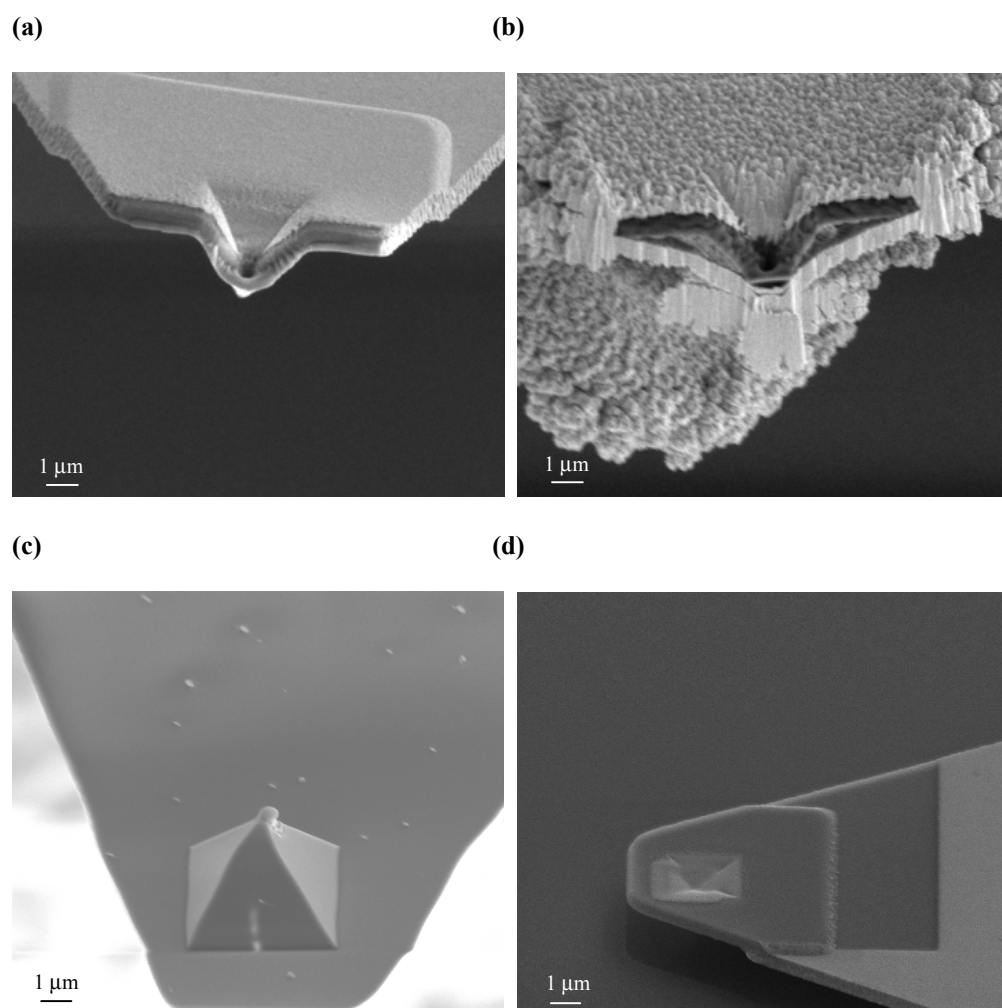


Figure 3. SEM images demonstrating FIB aperture milling. (a) Hollow PNP-TR probe, (b) reverse side of NP cantilever after circular cut-away, (c) reverse side of NP cantilever after aperture milling and (d) NP pyramidal tip after aperture milling.



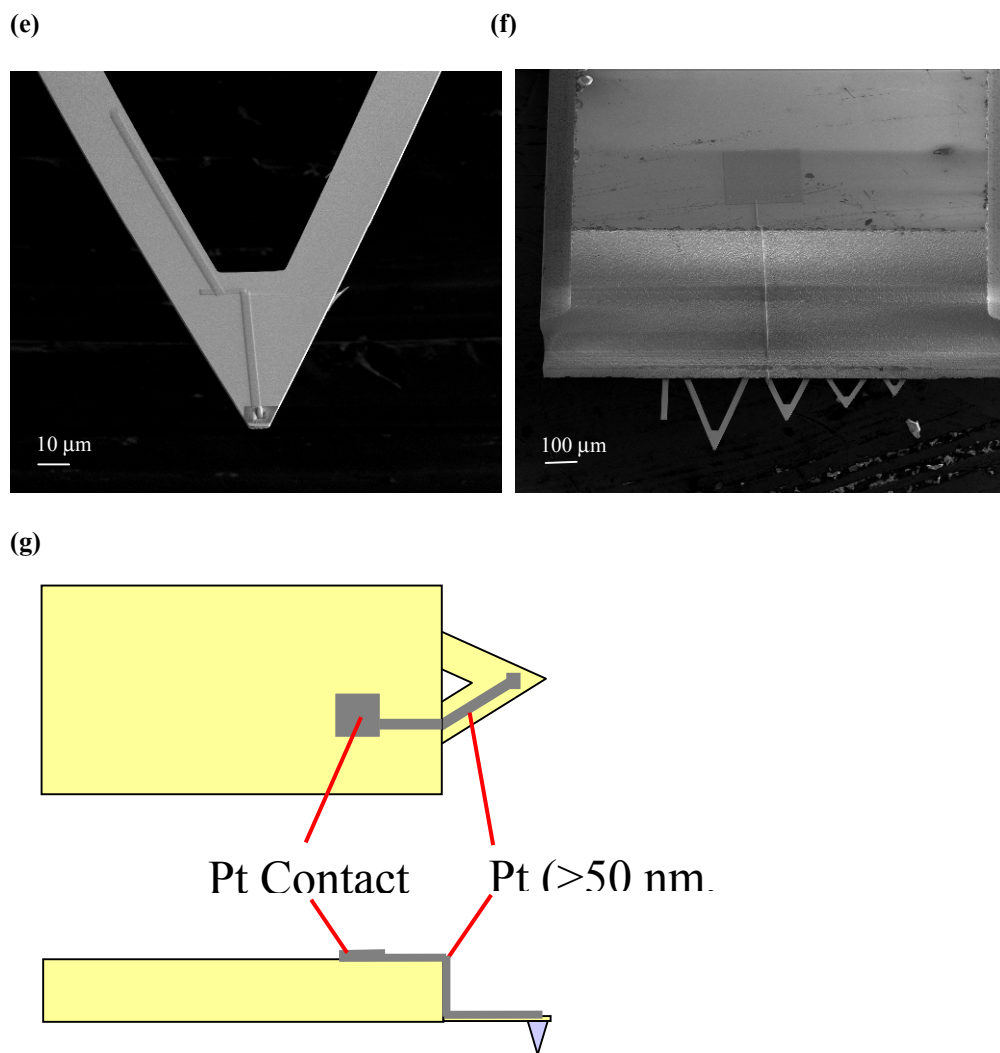


Figure 4. SEM images demonstrating platinum deposition. Cross-sections through probes after electrochemical deposition of Pt for 1h at (a) 0.1 V vs. Ag and (b) -0.4 V vs. Ag. Images (c) – (f) depict probes after directed beam-assisted platinum deposition. (c) Pyramidal tip, (d) reverse side of cantilever with the hollow filled with platinum, (e) connection lines of platinum deposited along the reverse side of the cantilever, (f) connection lines and connection pad on the probe body and (g) schematic depiction of platinum connections.

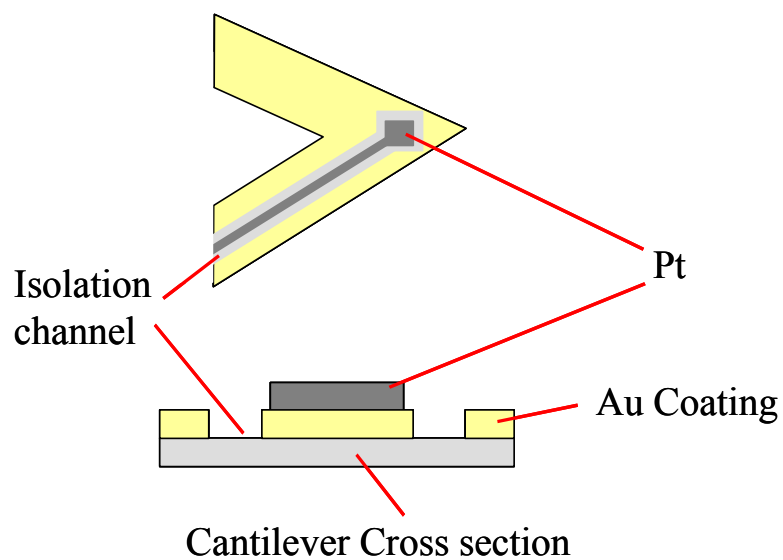


Figure 5. Schematic illustration of FIB milled isolation channels

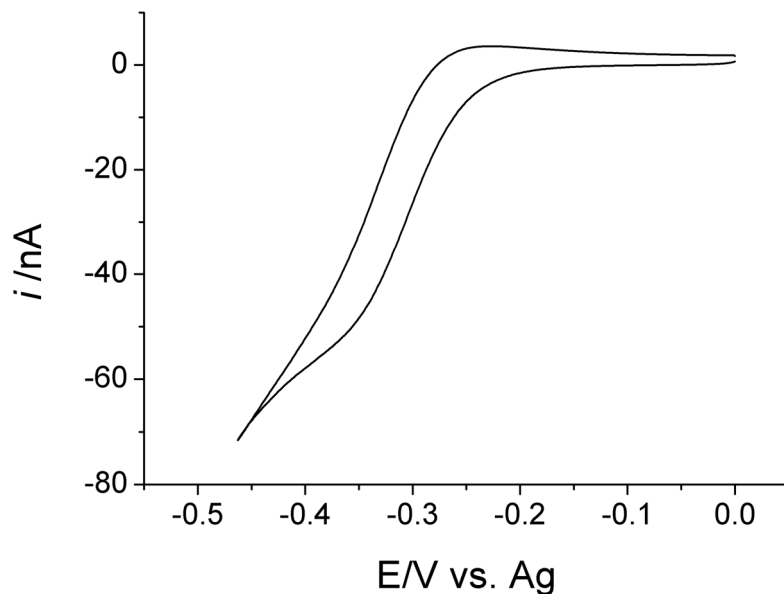


Figure 6. Cyclic voltammetry at a scan rate of 10 mV s^{-1} of fabricated probe immersed in $1 \text{ mM Ru(NH}_3)_6^{3+}/0.1 \text{ M KNO}_3$ (end of cantilever only exposed).

7 REFERENCES

- (1) Amemiya, S.; Bard, A. J.; Fan, F. R. F.; Mirkin, M. V.; Unwin, P. R. *Annual Review of Analytical Chemistry* **2008**, *1*, 95.
- (2) *Scanning Electrochemical Microscopy*; Bard, A. J.; Mirkin, M. V., Eds.; Marcel Dekker: New York, 2001.
- (3) Bard, A. J.; Li, X.; Zhan, W. *Biosensors & Bioelectronics* **2006**, *22*, 461.
- (4) Roberts, W. S.; Lonsdale, D. J.; Griffiths, J.; Higson, S. P. J. *Biosensors & Bioelectronics* **2007**, *23*, 301.
- (5) Diakowski, P. M.; Kraatz, H. B. *Chemical Communications* **2009**, 1189.
- (6) Wain, A. J.; Zhou, F. M. *Langmuir* **2008**, *24*, 5155.
- (7) Eckhard, K.; Etienne, M.; Schulte, A.; Schuhmann, W. *Electrochemistry Communications* **2007**, *9*, 1793.
- (8) Niu, L.; Yin, Y. H.; Guo, W. K.; Lu, M.; Qin, R. J.; Chen, S. H. *Journal of Materials Science* **2009**, *44*, 4511.
- (9) Macpherson, J. V.; Unwin, P. R. *Journal of Physical Chemistry* **1996**, *100*, 19475.
- (10) Jones, C. E.; Unwin, P. R.; Macpherson, J. V. *Chemphyschem* **2003**, *4*, 139.
- (11) Nagaiah, T. C.; Maljusch, A.; Chen, X. X.; Bron, M.; Schuhmann, W. *Chemphyschem* **2009**, *10*, 2711.
- (12) Nicholson, P. G.; Zhou, S.; Hinds, G.; Wain, A. J.; Turnbull, A. *Electrochimica Acta* **2009**, *54*, 4525.
- (13) Katemann, B. B.; Schuhmann, T. *Electroanalysis* **2002**, *14*, 22.
- (14) Laforge, F. O.; Velmurugan, J.; Wang, Y. X.; Mirkin, M. V. *Analytical Chemistry* **2009**, *81*, 3143.
- (15) Sun, P.; Zhang, Z. Q.; Guo, J. D.; Shao, Y. H. *Analytical Chemistry* **2001**, *73*, 5346.
- (16) James, P. I.; Garfias-Mesias, L. F.; Moyer, P. J.; Smyrl, W. H. *Journal of the Electrochemical Society* **1998**, *145*, L64.
- (17) Karrai, K.; Grober, R. D. *Applied Physics Letters* **1995**, *66*, 1842.
- (18) Schuhmann, W.; Schulte, A.; Etienne, M.; Turcu, F.; Fritsch, I. *Abstracts of Papers of the American Chemical Society* **2003**, 226, 196.
- (19) Etienne, M.; Anderson, E. C.; Evans, S. R.; Schuhmann, W.; Fritsch, I. *Analytical Chemistry* **2006**, *78*, 7317.
- (20) Katemann, B. B.; Schulte, A.; Schuhmann, W. *Chemistry-a European Journal* **2003**, *9*, 2025.
- (21) Katemann, B. B.; Schulte, A.; Schuhmann, W. *Electroanalysis* **2004**, *16*, 60.
- (22) Gardner, C. E.; Macpherson, J. V. *Analytical Chemistry* **2002**, *74*, 576A.
- (23) Macpherson, J. V.; Unwin, P. R. *Analytical Chemistry* **2001**, *73*, 550.
- (24) Burt, D. P.; Wilson, N. R.; Weaver, J. M. R.; Dobson, P. S.; Macpherson, J. V. *Nano Letters* **2005**, *5*, 639.
- (25) Dobson, P. S.; Weaver, J. M. R.; Holder, M. N.; Unwin, P. R.; Macpherson, J. V. *Analytical Chemistry* **2005**, *77*, 424.
- (26) Shin, H.; Hesketh, P. J.; Mizaikoff, B.; Kranz, C. *Sensors and Actuators B-Chemical* **2008**, *134*, 488.
- (27) Shin, H.; Hesketh, P. J.; Mizaikoff, B.; Kranz, C. *Analytical Chemistry* **2007**, *79*, 4769.
- (28) Kueng, A.; Kranz, C.; Mizaikoff, B.; Lugstein, A.; Bertagnolli, E. *Applied Physics Letters* **2003**, *82*, 1592.
- (29) Abbou, J.; Demaille, C.; Druet, M.; Moiroux, J. *Analytical Chemistry* **2002**, *74*, 6355.
- (30) Anne, A.; Cambril, E.; Chovin, A.; Demaille, C.; Goyer, C. *Acs Nano* **2009**, *3*, 2927.

- (31) Fasching, R. J.; Tao, Y.; Prinz, F. B. *Sensors and Actuators B-Chemical* **2005**, *108*, 964.
- (32) Pust, S. E.; Salomo, M.; Oesterschulze, E.; Wittstock, G. *Nanotechnology* **2010**, *21*.
- (33) Menozzi, C.; Gazzadi, G. C.; Alessandrini, A.; Facci, P. *Ultramicroscopy* **2005**, *104*, 220.
- (34) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2 ed.; Wiley: New York, 2001.
- (35) Birkin, P. R.; SilvaMartinez, S. *Analytical Chemistry* **1997**, *69*, 2055.