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Characterization of Nanopipet-Supported ITIES Tips for Scanning Electrochemical Microscopy of Single Solid-State Nanopores

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Abstract

Nanoscale scanning electrochemical microscopy (SECM) is a powerful scanning probe technique that enables high-resolution imaging of chemical processes at single nanometer-sized objects. However, it has been a challenging task to quantitatively understand nanoscale SECM images, which requires to accurately characterize the size and geometry of nanoelectrode tips. Herein, we address this challenge through transmission electron microscopy (TEM) of quartz nanopipets for SECM imaging of single solid-state nanopores by using nanopipet-supported interfaces between two immiscible electrolyte solutions (ITIES) as tips. We take advantage of the high resolution of TEM to demonstrate that laser-pulled quartz nanopipets reproducibly yield not only an extremely small tip diameter of ~30 nm, but also a substantial tip roughness of ~5 nm. The size and roughness of a nanopipet can be reliably determined by optimizing the intensity of the electron beam not to melt or deform the quartz nanotip without metal coating. Electrochemically, the nanoscale ITIES supported by a rough nanotip gives higher amperometric responses to tetrabutylammonium than expected for a 30 nm-diameter disk tip. The finite element simulation of sphere-cap ITIES tips accounts for the high current responses and also reveals that the SECM images of 100 nm-diameter Si₃N₄ nanopores are enlarged along the direction of the tip scan. Nevertheless, spatial resolution is not significantly compromised by a sphere-cap tip, which can be scanned in closer proximity to the substrate. This finding augments the utility of a protruded tip, which can be fabricated and miniaturized more readily to facilitate nanoscale SECM imaging.

Graphical Abstract

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Theoretical model for finite element simulation.

The power of nanoscale scanning electrochemical microscopy^{1,2} (SECM) to image the chemical reactivity of single nanometer-sized objects is highly attractive for various applications including nanomaterial characterization. Such applications are exemplified by recent studies of single solid-state nanopores³ and single metal nanoparticles.^{4–7} Nanoscale SECM imaging, however, is still a challenging task owing to several technical difficulties, some of which were recently recognized and resolved,⁸ i.e. thermal drift,⁹ tip damage,¹⁰ and adventitious contamination.^{7,11} By contrast, a long-standing challenge is to reliably characterize the size and geometry of nanoelectrode tips,¹ which is required to quantitatively interpret SECM images. In fact, SECM was developed for more reliable in-situ characterization of the size and geometry of nanotips than other electrochemical methods.¹² Moreover, AFM¹³ and scanning electron microscopy¹⁰ (SEM) are useful, especially when a tip is protruded or recessed to complicate its geometry. A higher resolution, however, is required to characterize very small tips (<100 nm) in detail.

Herein, we report on high-resolution transmission electron microscopy (TEM) of quartz nanopipet tips as supports of interfaces between two immiscible electrolyte solutions (ITIES) for nanoscale SECM imaging. TEM enables the characterization of <100 nm-diameter quartz nanopipets without metal coating,^{14,15} which is usually made on nanopipets for SEM to inhibit charging and reduce thermal damage^{3,14,16,17} although quartz nanopipets without metal coating were also imaged by SEM and scanning transmission electron microscopy.¹⁸ The TEM method was employed to examine carbon-filled nanopipets for SECM¹⁹ in addition to non-filled nanopipets, which were further characterized by conductivity measurement in the aqueous electrolyte solution^{18,20,21} and cyclic voltammetry at the nanopipet-supported ITIES.²¹ Accordingly, this work is the first to assess the size and geometry of a nanopipet-supported ITIES by SECM with knowledge about the size and geometry of the nanopipet tip characterized by TEM. This assessment augments the reliability of nanopipet-supported ITIES, which found various electroanalytical applications^{22–24} including high-resolution SECM imaging^{3,25,26} and electrochemical sensing.^{27,28} In addition, we optimize the intensity of the electron beam not to melt or deform insulating nanopipets during TEM characterization. The electron beam of SEM was previously used to melt quartz nanotips to smaller sizes.²⁹

In this study, high-resolution TEM of quartz nanopipet tips allows us to quantitatively understand SECM images of single solid-state nanopores. Specifically, we image a nanoporous Si₃N₄ membrane by employing a nanopipet-supported ITIES tip (Figure 1A), where the amperometric current response based on the transfer of a target ion (tetrabutylammonium; TBA⁺) is lowered over the pore wall by the negative feedback effect and is recovered over a nanopore to resolve it (Figure 1B). The Si₃N₄ membrane is

perforated by a periodic array of 100 nm-diameter nanopores in contrast to randomly distributed nanopores with various shapes and smaller sizes (~50 nm) as imaged in our previous study.³ Moreover, we characterize quartz nanopipets by high-resolution TEM to determine a tip diameter of ~30 nm and a tip roughness of ~5 nm. Information about the size and geometry of nanopores and nanotips facilitates the finite element analysis of SECM images to reveal that the nanoscale ITIES supported by a rough nanopipet tip is represented by sphere-cap geometry and is also disturbed near nanopores, which are enlarged in their SECM images along the direction of the tip scan. High spatial resolution, however, is still achieved by scanning a sphere-cap tip at a very short distance from the substrate.

EXPERIMENTAL SECTION

Chemicals and Materials

Tetradodecylammonium (TDDA) bromide, 1,2-dichloroethane (DCE; >98%), tetrabutylammonium chloride, potassium chloride, and *N*-dimethyltrimethyl silylamine (Selectophore grade) were purchased from Sigma-Aldrich (Saint Louis, MO). Potassium tetrakis(pentafluorophenyl)borate (TFAB) was obtained from Boulder Scientific Company (Mead, CO). Isopropyl alcohol was obtained from J. T. Baker (Phillipsburg, NJ). All reagents were used as received. The TFAB salt of TDDA was prepared by metathesis.³⁰ 5 mM TBACl was dissolved with 0.3 M KCl in 18.3 MΩ cm deionized water obtained from a Milli-Q Advantage A10 water purification system (EMD Millipore, Billerica, MA) with a TOC value of 2 ppb as measured by using an internal online TOC monitor. The Milli-Q system was fed with the water (15.0 MΩ·cm) purified from tap water by using Elix 3 Advantage (EMD Millipore). The resulting solution was passed through a 0.02 μm filter (Whatman Anotop syringe filter, Sigma-Aldrich) before its use for SECM imaging of a nanoporous Si₃N₄ membrane (21585-10, Ted Pella, Redding, CA).

Tip Fabrication

Quartz nanopipet tips were fabricated as reported elsewhere^{3,9} with some modifications. A quartz capillary (O.D. 1 mm, I.D. 0.7 mm, 10 cm long, Sutter Instrument, Novato, CA) was air blow cleaned before pulling and was pulled in a CO₂-laser puller (Model P-2000, Sutter Instrument). Approximately 30 nm-diameter nanopipets were obtained by running the line of a standard program³¹ with parameters of heat = 700, filament = 4, velocity = 60, delay = 145, and pull = 125.

Modifications were made for cleaning and silanizing nanopipets. Specifically, pulled nanopipets were cleaned for three minutes in a plasma cleaner (PDC-32G, Harrick Plasma, Ithaca, NY). Ar was used as a carrier gas and passed through a water-filled bubbler to introduce water vapor into the chamber. The treatment of nanopipets with radio-frequency-generated Ar/H₂O plasma not only cleans the quartz surface, but also introduces hydroxyl groups on the surface³² for more reproducible silanization. The clean nanopipets were dried for >1.5 hours under vacuum in a mini vacuum desiccator (Bel-Art Products, Pequannock, NJ) and then silanized by introducing 50 μL of *N*-dimethyltrimethyl silylamine into the desiccator. In this study, the mini desiccator was placed in a gas-purge desiccator cabinet (Bel-Art Products) filled with dry nitrogen. A silanization time was adjusted within a narrow

range of 35 ± 5 min depending on the temperature and humidity of the atmosphere. After silanization, a vacuum was applied to the mini desiccator for ~ 1 min to remove the extra silanization agent.

TEM Characterization

As-pulled quartz nanopipets were imaged by using a JEOL JEM-2100F microscope operating at 200 kV accelerating voltage. The intensity of the electron beam was optimized by adjusting “brightness” not to melt or deform a nanopipet tip. In addition, we employed the largest condenser aperture and intermediate objective apertures.

SECM Measurement

A homebuilt instrument³ with an isothermal chamber⁹ was used for nanoscale SECM imaging. A nanoporous Si_3N_4 membrane was cleaned for six minutes in piranha and for 11 minutes in Milli-Q water, and wet with isopropanol to prevent the formation of residual air bubbles in nanopores in the electrolyte solution³³ (Figure 1). Pt and Ag/AgCl wires were placed inside and outside of an organic-filled nanopipet (Figure 1A). Electrochemical measurements were carried out by using a commercial potentiostat (CHI 900A, CH Instruments, Austin, TX).

RESULTS AND DISCUSSION

High-Resolution TEM of Quartz Nanopipets

We employed high magnifications of TEM to evaluate not only inner and outer diameters of quartz nanopipet tips ($2a$ and $2r_g$, respectively, in Figure 1B), but also their roughness. Specifically, we changed magnifications from $\times 50,000$ to $\times 200,000$ to obtain consistent inner and outer tip diameters of ~ 30 and ~ 42 nm, respectively (Figures 2A–2C). The corresponding RG value of $r_g/a = 1.4$ also agreed with the ratio of the outer diameter of a quartz capillary with respect to its inner diameter (1.0 mm and 0.7 mm, respectively). The consistent diameters and shape of a tip at various magnifications ensure that the electron beam did not melt or deform the tips without metal coating. Moreover, a pair of nanopipets pulled from the same capillary had nearly identical diameters and complementary shapes, which also supports that the tips were not melted or deformed by the electron beam. It should be noted that the TEM images were darkened intentionally by employing the electron beam that had the sufficiently low intensity not to melt or deform the nanotips. The focal plane of the electron beam was adjusted to the central plane of a nanopipet as shown in Figures 2A–2C to measure inner diameters of 30 ± 2 nm for 12 quartz nanopipets with $RG = 1.4$ pulled by using the standard program.³¹ By contrast, the electron beam was focused on the front side of a nanotip to estimate its roughness of ~ 5 nm (Figure 2D). The roughness of a borosilicate nanopipet tip was imaged previously by SEM, which required a metal-coated nanopipet with a larger diameter of ~ 150 nm.¹⁷

The tip of a quartz nanopipet can be melted or deformed when the intensity of the electron beam is too high. This artifact was not pointed out in previous TEM studies of quartz nanopipets, which look deformed in some images. An intact nanopipet tip was imaged at various magnifications (Figures 2A–2C) and then exposed to a more intense electron beam,

which increased the inner tip radius, a , from 15 nm to 24 nm (Figure 3A). Such an outward deformation of a quartz nanopipet tip was observed also in the previous TEM study.¹⁸ Another tip (Figure 3B) was more seriously deformed when it was imaged by employing an even more intense electron beam to obtain a bright image at a higher magnification. The geometry of this deformed tip is very similar to the hourglass shape of a quartz nanopipet tip imaged by helium ion microscopy.³⁴ Also, the TEM image of a carbon-filled nanopipet tip showed an hourglass shape.¹⁹

Nanopipet-Supported ITIES Tips

In this study, quartz nanopipets were filled with an electrolyte solution of DCE to support nanoscale ITIES in the aqueous electrolyte solution of TBA⁺ as a target ion (Figure 1). A Pt electrode was placed in an organic-filled nanopipet and biased against a Ag/AgCl electrode in the aqueous solution to drive the diffusion-limited transfer of TBA⁺ across the nanopipet-supported ITIES. When the tip was positioned in the bulk solution, the corresponding amperometric limiting current, $i_{T,\infty}$, was given by

$$i_{T,\infty} = 4xzFDc_0a \quad (1)$$

where x depends on the tip geometry and equals to 1.18³⁵ for a disk tip with $RG = 1.4$, $z (= +1)$ is the charge of the transferred ion, $D (= 5.1 \times 10^{-6} \text{ cm}^2/\text{s})$ and $c_0 (= 5 \text{ mM})$ are the diffusion coefficient and concentration of the transferred ion in the bulk solution, respectively.

We found that a nanopipet-supported ITIES often yielded a higher limiting current in the bulk solution than expected from eq 1 for a disk-shaped ITIES that is flush with the tip of a nanopipet. Specifically, we studied 13 nanopipet tips to find that 10 tips gave limiting currents that are higher than a $i_{T,\infty}$ value of 17.5 pA expected from eq 1 for a disk-shaped tip with a radius of 15 nm as determined for nanopipets by TEM. Experimental $i_{T,\infty}$ values varied from ~20 pA to ~30 pA, which are likely dependent on the roughness of a nanopipet tip as well as the degree of tip silanization. When a disk-shaped ITIES is assumed, these currents correspond to inner diameters of 34 nm–52 nm, which are too large in comparison with the inner diameters of nanopipet tips determined by TEM ($30 \pm 2 \text{ nm}$). These higher tip currents are attributed to the protrusion of the ITIES from the tip of a nanopipet (see below). It should also be noted that a few tips gave limiting currents that are lower than expected for a disk tip, which is attributed to the recession of the ITIES from the nanopipet tip.

The higher currents at nanopipet-supported ITIES in the bulk solution are attributed to the sphere-cap geometry of the ITIES protruded from the tip of a pipet³⁶ as quantitatively supported by the finite element simulation (Supporting Information). For instance, a limiting current of 20.3 pA was obtained with a nanopipet-supported ITIES tip used for SECM imaging (see below) and was consistent with the current obtained by the finite element simulation of a sphere-cap tip with $a = 15 \text{ nm}$, $RG = 1.4$, and $h/a = 0.18$ (h is the height of the sphere cap; see Figure 1B), thereby yielding $x = 1.38$ in eq 1. The actual height of this sphere-cap tip is only 2.7 nm, which is smaller than the roughness of the tip end estimated

by TEM. By contrast, a much higher $i_{T,\infty}$ value of 27.9 pA was obtained with a nanopipet-supported ITIES tip for SECM imaging (see below) and was simulated for a sphere-cap tip with $a = 15$ nm, $RG = 1.4$, and $h/a = 0.85$ (i.e. $h = 12.1$ nm), where $x = 1.89$ in eq 1. It should be noted that the knowledge of nanopipet inner and outer diameters as obtained by TEM was essential to determine the height of the sphere-cap ITIES from a limiting current by the finite element simulation.

SECM Imaging of Single Si_3N_4 Nanopores

We employed nanopipet-supported ITIES tips for SECM to quantitatively image ion transport through single Si_3N_4 nanopores. In this study, we imaged a periodic array of circular nanopores with a diameter of 100 nm and a pore–pore separation of 100 nm as characterized by TEM (Figure 4) to facilitate the finite element analysis of their SECM images (see below). The nanopores were formed through a 200 nm-thick Si_3N_4 membrane, which was robust enough to self-stand in the aqueous electrolyte solution (Figure 1A). The Si_3N_4 membrane was also flat and oriented perpendicular to the tip, which can be scanned at a constant height without contact with the membrane surface over an area of $300 \text{ nm} \times 600 \text{ nm}$. The constant tip height was maintained by employing an isothermal chamber, which prevented the thermal drift of the tip position.^{3,9} A single nanopipet was used to study 2–12 different locations of a single membrane. Overall, we studied 13 membranes and obtained good images with 10 membranes.

Figure 5A shows a representative SECM image of an array of 100 nm-diameter Si_3N_4 pores, where the diffusion-limited tip current, i_T , was normalized against the tip current in the bulk solution, $i_{T,\infty}$. The normalized tip current, $i_T/i_{T,\infty}$, was reduced to ~ 0.70 by the negative feedback effect from the insulating membrane surface at $x = y = 0$, where the tip approached initially. The normalized tip current was recovered to ~ 0.90 as the tip was scanned over the center of each nanopore, which mediated the flux of TBA^+ to the ITIES tip (Figure 1B). The periodicity of the nanopore array expected from the TEM image (Figure 4) was also seen in the SECM image. By contrast, nanopores in the SECM image look larger than their actual diameter and also slightly elongated along the direction of the tip scan, i.e. the x -direction. The diameter of a nanopore in the SECM image should be larger than its actual diameter by the tip diameter,³ because the tip current is enhanced by the flux of TBA^+ from the nanopore even when the edge of the ITIES tip is positioned over the edge of a nanopore. This approximation was validated by the SECM image in the y direction, although the ITIES was slightly protruded from the nanopipet tip by $h/a = 0.18$ to yield $i_{T,\infty} = 20.3$ pA in eq 1 (see above). This result also implies that the SECM images of nanopores were enlarged along the x direction as ensured by the finite element analysis (see below).

The finite element analysis indicates that the SECM image of a circular nanopore is enlarged along the x direction and is consistent with simulation in the y direction. In this model, one cylindrical nanopore was considered and imaged with a sphere-cap tip (Figure S-1A). A nanopipet–membrane distance, d , of 14.25 nm (Figure 1B) was employed in the simulation so that the simulated $i_T/i_{T,\infty}$ value increased from ~ 0.70 over the insulating membrane surface to ~ 0.90 over the center of the nanopore as observed experimentally along black lines across a nanopore in Figure 5A. The simulated tip current, however, was systematically

lower than the experimental current when the tip was scanned toward and away from the edge of a nanopore in the x direction, thereby elongating the experimental line scan (see red circles in Figure 5B for higher experimental currents). This systematic deviation contrasts to the random deviation of the experimental tip current from the simulated tip current over the center of the nanopore. By contrast, no elongation was observed along the y direction (Figure 5C). It is unclear why the SECM image of nanopores looks elongated only in the x direction. However, this asymmetry of circular nanopores in their SECM images can not be attributed to the drift of a tip positioner, which was mechanically locked.^{7,8} Moreover, the SECM image of a nanopore was always elongated in the x direction when nanopore membranes were rotated with respect to the z direction. This result indicates that the elongation is not due to the presence of adjacent nanopores that can asymmetrically surround the central nanopore with respect to x and y directions. In fact, the finite element simulation showed no asymmetry between SECM line scans over a nanopore in x and y directions although the pore was surrounded by six closest nanopores asymmetrically between x and y directions. This simulation result ensured that adjacent nanopores were located too far from the imaged nanopore to affect the tip current.

Single Nanopore Imaging with Largely Protruded ITIES Nanotips

We also imaged single Si_3N_4 nanopores when the nanopipet-supported ITIES was largely protruded, i.e. $h/a = 0.85$. The large protrusion was noticeable, because a tip current of 27.9 pA in the bulk solution was much higher than expected for a disk-shaped ITIES supported by a nanopipet with a typical tip diameter of 30 nm. In fact, the experimental $i_{T,\infty}$ value corresponded to an inner diameter of 48 nm for a disk-shaped tip with $RG = 1.4$ in eq 1. However, the resultant SECM image of single nanopores (Figure 6A) yielded much higher spatial resolution than expected for a 48 nm-diameter disk-shaped tip.

We employed the finite element method to better understand the SECM image of single nanopores as obtained with a largely protruded nanotip. The simulation of a sphere-cap tip with $h/a = 0.85$ accounted for not only the high $i_{T,\infty}$ value, but also the tip current during imaging when a nanopipet–membrane distance, d , of 16.8 nm was used. This distance corresponds to an actual separation, $d - h$, of only 4.7 nm between the membrane and the highest point of the sphere-cap ITIES (Figure 1B). The close distance of the sphere-cap tip from the membrane contributed to the high resolution of the SECM image as represented by line scans over the nanopore along the black lines in Figure 6A. Specifically, the corresponding experimental line scans in both x and y directions (Figures 6B and 6C, respectively) agreed well with line scans simulated for a sphere-cap tip with $a = 15$ nm and $h = 12.1$ nm, although the experimental tip current was systematically higher than the simulated current when the tip was scanned toward or away from the edge of the nanopore in the x direction (see red circles in Figure 6B). Such a systematic rather than random deviation was observed also when a slightly protruded tip was used (Figure 5B).

A Comparison between Hemispherical and Disk Tips

We performed the finite element simulation to compare the spatial resolution of SECM between hemispherical and disk tips ($h/a = 1$ and 0, respectively). In this simulation, we considered SECM line scans of two substrates. First, we simulated SECM line scans of a

single nanopore (Figure S-1A) based on the negative feedback mechanism as reported in this work. In addition, we considered SECM line scans of a disk-shaped conductor embedded in an insulating substrate (Figure S-1B) to examine the positive feed-back mechanism.³⁷ In this case, the tip current is based on the electrolysis of a redox molecule and is enhanced by the conductor, which converts the tip-generated species to the original redox molecule.

Figure 7A shows SECM line scans of a nanopore with a disk-shaped tip as well as a hemispherical tip. A tip-substrate distance of $d/a = 0.75$ was selected for the disk tip to yield a normalized current of ~ 0.7 over the insulating surface. A nearly identical normalized current was obtained by positioning the hemispherical tip at $d/a = 1.3$ over the insulating surface, from which the highest point of the hemispherical tip was separated by only $d/a - h/a = 0.3$. These conditions mimic our experiments, where the tip approached to the insulating membrane surface until the tip current dropped to $\sim 70\%$ (Figures 5A and 6A). The simulated line scans of a nanopore show that the spatial resolution of the hemispherical tip (red circles) is comparable to that of the disk tip with the same radius (black circles). Noticeably, a higher current of the disk tip over the nanopore yielded a higher image contrast. A comparable image contrast was obtained by scanning the hemispherical tip at a shorter distance of $d/a = 1.1$ (blue circles). In this case, the highest point of the hemispherical tip was positioned at a very short normalized distance of 0.1 from the substrate surface, although, the tip of the cylindrical support (i.e. nanopipet) was still positioned farther from the substrate surface than the disk tip at $d/a = 0.75$.

SECM line scans of a conductive nanodisk were simulated by the finite element method to demonstrate that the spatial resolution based on the positive feedback mechanism is similar between a hemispherical tip (red circles in Figure 7B) and a disk-shaped tip with the same radius (black circles). In this simulation, both tips were positioned at different distances from the substrate surface so that their normalized current responses were nearly identical (i.e. ~ 0.70) over the insulating surface surrounding the nanodisk. The current responses of both tips were enhanced over the conductive disk by the positive feedback effect to yield similar spatial resolutions. By contrast, the image contrast of the disk tip at this distance of $d/a = 1.3$ was lower than that of the hemispherical tip at the corresponding distance of $d/a = 0.75$, where the highest point of the hemispherical tip was positioned very close to the conductive disk, i.e. $d/a - h/a = 0.3$. Image contrast was improved for the disk tip by scanning it a little closer to the substrate, i.e. $d/a = 0.60$ (blue circles). The corresponding spatial resolution, however, was still similar to the spatial resolution of the hemispherical tip, thereby confirming that the spatial resolution of disk and hemispherical tips is mainly determined by the tip radius.

CONCLUSIONS

In this study, we demonstrated a powerful combination of TEM of a nanopipet with SECM of a nanopipet-supported ITIES tip to advance quantitative SECM imaging at the nanoscale. The intrinsic size and roughness of quartz nanopipet tips were observable by TEM with higher resolution in this study than by SEM in previous studies,^{3,14,16,17} not only because TEM does not need the metal coating of a nanopipet, but also because we optimized the intensity of the electron beam for TEM not to melt or deform the insulating nanotip at high

magnification.^{18,19,29,34} Moreover, a periodic array of 100 nm-diameter nanopores was imaged in this study in contrast to our previous study of randomly distributed nanopores with various sizes and shapes.³ Information about the size and geometry of nanotips and nanopores was crucial for the reliable finite element analysis of SECM images, where the elongation of circular nanopores along the direction of the tip scan was identified.

In addition, this study compared protruded SECM tips for high-resolution imaging with disk tips, which are often desired. We ensured both experimentally and theoretically that spatial resolution is not compromised by using sphere-cap tips, which can be scanned in close proximity to a substrate without tip–substrate contact. This advantage of a sphere-cap tip originates from the protrusion of the tip from the insulating sheath in contrast to a flush disk tip, where the insulating sheath contacts a substrate to limit the closest tip–substrate distance.³⁸ To our knowledge, this work is the first to quantitatively compare tips with different geometries for SECM imaging. It should be considered in future studies how the spatial resolution of SECM depends on the exact geometry of a protruded (or even recessed) tip, which can be more readily fabricated to facilitate high-resolution SECM imaging and also miniaturized to yield extremely small tips of down to a few nanometers.^{39,40}

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
 (A) An SECM cell with a nanoporous Si₃N₄ membrane and a DCE-filled nanopipet tip. (B)
 Constant-height SECM imaging of single Si₃N₄ nanopores.

Figure 2. TEM images of a quartz nanopipet at (A) $\times 50,000$, (B) $\times 100,000$, and (C) $\times 200,000$ as well as another nanopipet at (D) $\times 120,000$, where a white bar represents 5 nm roughness of the tip.

Figure 3. TEM images of nanopipets deformed by the electron beam at (A) $\times 80,000$ and (B) $\times 100,000$.

Figure 4.
TEM images of a nanoporous Si₃N₄ membrane at (A) $\times 12,000$ and (B) $\times 60,000$.

Figure 5.

(A) A 300 nm × 600 nm SECM image of single Si₃N₄ nanopores as obtained with a sphere-cap nanopipet tip in 1 M KCl containing 5 mM TBACl. Probe scan rate, 100 nm/s in the *x* direction. Cross sections (circles) as indicated by black lines in Part (A) along (B) *x* and (C) *y* directions. Red circles indicate the experimental data points that systematically deviate from simulation to apparently broaden the nanopore image in the *x* direction. Solid lines represent simulation results with $a = 15$ nm, $r_g = 21$ nm, $h = 2.7$ nm, and $d = 14.25$ nm (See Figure 1B). Dashed lines locate the edges of a 100 nm-diameter pore.

Figure 6.

(A) A 300 nm × 600 nm SECM image of single Si_3N_4 nanopores as obtained with a sphere-cap nanopipet tip in 1 M KCl containing 5 mM TBACl. Probe scan rate, 100 nm/s in the x direction. Cross sections (circles) as indicated by black lines in Part (A) along (B) x and (C) y directions. Red circles indicate the experimental data points that systematically deviate from simulation to apparently broaden the nanopore image in the x direction. Solid lines represent simulation results with $a = 15$ nm, $r_g = 21$ nm, $h = 12.1$ nm, and $d = 16.8$ nm (See Figure 1B). Dashed lines locate the edges of a 100 nm-diameter pore.

Figure 7.

Finite element simulation of SECM line scans with disk and hemispherical tips over (A) single nanopore with a radius of $3a$ (dotted lines) and a length of $6a$ and (B) single conductive nanodisk with a radius of $3a$ (dotted lines). The lateral tip position was normalized against the tip radius, a .