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Spatially Resolved Detection of a Nanometer-Scale Gap by Scanning Electrochemical Microscopy

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Abstract

Nanowires with nanometer-scale gaps are an emerging class of nanomaterials with potential applications in electronics and optics. Here we demonstrate that the feedback mode of scanning electrochemical microscopy (SECM) allows for spatially resolved detection of a nanogap on the basis of its electrical conductivity. A gapped nanoband is employed as a model system to describe a mechanism of a unique feedback effect from a nanogap. Interestingly, both experiments and numerical simulations confirm that a peak current response is obtained when an SECM tip is laterally scanned above an insulating nanogap formed in an unbiased nanoband. On the other hand, no peak current response is expected for a highly conductive nanogap, which must be extremely narrow or filled with highly conductive molecules for efficient electron transport.

Here we report on a novel application of scanning electrochemical microscopy (SECM)^{1, 2} to spatially resolved detection of a nanometer-scale gap formed in a nanowire. A gapped nanowire is an emerging class of nanomaterial that has attracted tremendous attentions because of its potential applications in electronics and optics.^{3, 4} An important progress during the past few years is that high-throughput and low-cost chemical methods have been developed to create a gapped nanowire without traditional lithography.^{5–10} Electrical transport through a nanogap can be also tuned chemically by controlling the sizes of the gap⁶ or by bridging the gap with conductive molecules⁸ or polymers.^{5, 10} Conventional methods of electrical characterization of a gapped nanowire, however, require good ohmic contact of both ends of a single nanowire with lithographically fabricated electrodes for an external bias and a current measurement.^{5, 6, 8, 10} Moreover, these methods are not useful to resolve multiple nanogaps in a nanowire.

SECM is a powerful technique for electrochemical characterization of nanomaterials and nanosystems at high spatial resolution.^{2, 11} Recently, we employed the feedback mode of SECM to drive and probe electron transport at an individual nanoband, which is not attached to a contact electrode and is electrically isolated on an insulating substrate in an electrolyte solution (Figure 1).^{12, 13} Specifically, a redox molecule (blue spheres) is electrolyzed at the tip of an ultramicroelectrode probe that is brought to the proximity of a nanoband. Electrolysis of the tip-generated species (orange spheres) at the nanoband surface regenerates the original redox species, which is detected amperometrically at the tip. Importantly, mediator regeneration at the surface of an unbiased nanoband drives electron transport through the nanoband and subsequent electrolysis of the original mediator at the exterior surface of the

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Supporting Information Available

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

nanoband. Thus, a nanogap in a nanoband is expected to limit the lateral electron transport and affect the tip current response.

This work describes the proof-of-concept experiment to enable spatially resolved detection of a nanogap by SECM in the feedback mode. Interestingly, we find that a unique peak current response is obtained at an SECM probe when the tip is scanned above an insulating nanogap in an unbiased nanoband. Numerical simulations reveal a mechanism of the SECM feedback response to an insulating nanogap. Moreover, we discuss how a tip current is affected by nanogap conductivity, which depends on electron transport properties of the nanogap.

EXPERIMENTAL SECTION

Gap-free Au nanobands were fabricated on the SiO₂/Si substrate by electron-beam lithography and characterized in detail as reported elsewhere.¹³ A gap was formed by gradual degradation of a nanoband during storage. Figure 2 shows an SEM image of the 37 nm-wide nanogap formed at 22 μm from an end of a 50 μm-long Au nanoband. Only the 37 nm-wide gap was detected by SEM and AFM. The lack of a gap in another 50 μm-long nanoband as studied for a comparison was confirmed by SEM and AFM. The SEM and AFM studies also demonstrate non-uniform width and height of the nanobands, respectively. While the gapped nanoband is uniform around the nanogap (Figure 2), the band width varies between 43 and 89 nm along the longest axis toward the ends. The width of the gap-free nanoband also varies between 38 and 66 nm. These variations are due to the degradation because the width of original nanobands was uniformly 100 nm. The height of degraded nanobands determined by AFM also varies (between 34 and 50 nm) and is lower than the height of original nanobands (between 43 and 51 nm).¹³

SECM experiments were conducted by employing a commercial SECM instrument with closed-loop piezoelectric motors (CHI 910B, CH Instruments, Austin, TX, USA) to control the position of a Pt disk probe at nanometer scale. The inner and outer tip radii of 1.0 and 10.0 μm, respectively, were determined from current approach curves at an insulating Teflon substrate^{14, 15} and also confirmed by optical microscopy. A 1 mm-diameter AgCl-coated Ag wire served as a reference/counter electrode. The gapped or gap-free nanoband was placed in a two-electrode cell such that the longest axis of the nanoband is parallel to the *x*-direction of the piezoelectric motor (Figure 1). The tip was positioned above a nanoband as described elsewhere.¹³ The cell was filled with 0.1 KCl containing 2 mM Ru(NH₃)₆Cl₃ (Strem Chemicals, Newburyport, MA, USA) prepared with 18.3 MΩ·cm deionized water (Nanopure, Barnstead, Dubuque, IA).

RESULTS AND DISCUSSION

SECM-Based Detection of a Nanogap

We investigated the gapped nanoband (Figure 2) by SECM to find that the gap gives a peak current response at the tip (Figure 3a). In this SECM line scan experiment, the tip potential was set at −0.4 V vs Ag/AgCl to give steady-state tip current, i_T , based on diffusion-limited reduction of Ru(NH₃)₆³⁺. When the tip was positioned far from the substrate surface, the tip current, $i_{T,\infty}$, was given by

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

where n is the number of electrons in the tip reaction ($n = 1$ for Ru(NH₃)₆³⁺), F is Faraday constant, D and c are the diffusion coefficient and concentration of Ru(NH₃)₆³⁺ in the bulk

aqueous solution, and a is the tip radius. The tip current decreased to 56 % of $i_{T,\infty}$ (at $x = 0$ in Figure 3a) when the tip was positioned at 1.1 μm from the insulating SiO_2 surface, which hinders diffusion of $\text{Ru}(\text{NH}_3)_6^{3+}$ to the tip. As the tip was scanned laterally above the gapped nanoband along its longest axis, the tip current was enhanced by the feedback effect at the nanoband surface to give peak-shaped responses at three positions ($x = 22.12, 42.52$, and $68.32 \mu\text{m}$). The tip positions for the left and right peaks correspond to the edges of the gapped nanoband. The separation between these peaks is slightly smaller than the length of the nanoband as discussed later. The position of the middle peak agrees with the position of the nanogap, which is closer to the left edge than the right edge. Moreover, peak current responses were obtained only at the edges for the gap-free nanoband ($x = 22.8$, and $66.0 \mu\text{m}$ in Figure 3b). These results confirm that a peak current response was obtained when the tip was positioned above the nanogap.

A unique peak current response to a nanogap was simulated by employing the finite element method (Figure 4). A three-dimensional SECM diffusion problem with a nanoband under unbiased conditions was defined and solved by using COMSOL Multiphysics version 3.4 (COMSOL, Inc., Burlington, MA) as reported elsewhere.^{13, 16} A simulation report is attached as Supporting Information. The length, width, and height of the nanoband, and the tip–nanoband distance ($50a, 0.03a, 0.03a$, and a , respectively) are similar to those of the gapped and gap-free nanobands in the line scan experiments. An insulating gap with various sizes, w_g , was created in the middle of a nanoband to completely block direct electron transport between the two fragments of the gapped nanoband. When the insulating gap is smaller than the diameter of an SECM tip (solid lines with $w_g/2a = 0.0025$ and 0.25 in Figure 4), peak current responses are obtained at three tip positions, i.e., above the gap and outer edges. The largest peak current is obtained when the center of the disk-shaped tip is positioned just above the gap at $x = 0$. Remarkably, the tip current in line scans varies only a little with the gap size, which is varied by 2 orders of magnitude. This result indicates that redox cycling of mediator molecules in the gap is negligible. On the other hand, a larger gap that is comparable to the tip diameter (solid line with $w_g/2a = 1$ in Figure 4) gives a dip in the tip current while an even larger gap gives a deeper dip (solid line with $w_g/2a = 2.5$). These simulation results confirm that the 37 nm-wide gap employed in our experiment is small enough ($w_g = 0.037a$) to give a peak current response. Moreover, peak current responses were obtained only at the edges for a gap-free nanoband (dotted lines), which is also consistent with our experimental result.

The finite element simulation captures the main features of the experimental results. A quantitative comparison of the experimental and simulated line scans, however, reveals some differences between them. An experimental tip current above either a gapped or a gap-free Au nanoband (Figures 3a and b, respectively) is less enhanced in comparison to the tip current simulated for a Nernstian reaction at the corresponding nanoband with similar dimensions, thereby confirming slow electron transfer at our Au nanobands.¹³ Nevertheless, the peak currents at the edges of the real nanobands appear more significant than expected from the simulations. Moreover, the peak current at one edge of the real nanobands is higher than that at the other edge. We suggest that these differences in experimental and simulated peak currents near the edges are due to variations of width and height of the degraded nanobands toward the ends along their longest axis as demonstrated by SEM and AFM (see Experimental Section). These variations, which are not considered in the model, affect a tip feedback current.¹³ Importantly, the gapped nanoband is very uniform around the nanogap (Figure 2) so that the peak current response at the nanogap is not due to these variations.

A Mechanism of Nanogap Detection

A peak-shaped response to a nanogap, which is consistently demonstrated in both experiments and simulations, can be explained as follows (Figure 5). When the tip is positioned above a

small gap ($w_g < 2a$), both fragments of a gapped nanoband contribute to the process of mediator regeneration and electrolysis (the top of Figure 5). The tip-generated species, R, is effectively electrolyzed at the surface of both fragments just under the tip to regenerate original mediators, O. The exterior surface of each fragment is widely exposed to the bulk solution for electrolysis of the original mediators, thereby facilitating mediator regeneration to enhance the tip current. Overall, the tip current above a very small gap ($w_g/2a = 0.0025$ in Figure 4) is nearly identical to the tip current above the center of the gap-free nanoband with otherwise identical dimensions. In comparison, the tip current is smaller when the tip is positioned above the center of a fragment of a gapped nanoband. In this case, only the fragment under the tip contributes to the process of mediator regeneration and electrolysis (the middle of Figure 5), which is negligible on the other fragment isolated by an insulating gap.

Peak current responses are also observed around the edges of a gapped nanoband, which are due to less hindered diffusion of original mediators by the insulating sheath of the tip (the bottom of Figure 5). When a tip is positioned above an outer edge of a fragment of the gapped nanoband, the other edge of the same fragment is more widely available for electrolysis of original mediators in the bulk solution to significantly enhance the feedback effect. In contrast, simulated peak currents around the edges of a gap-free nanoband are much less pronounced, where a relatively large fraction of the whole nanoband surface is exposed to the bulk solution independent of the tip position. It should also be noted that a peak current response to an edge of a nanoband is obtained when the whole surface of the disk-shaped tip is positioned just above the inside of the edge. Therefore, the separation between two peaks is smaller than the total length of the nanoband ($46a$ and $50a$, respectively, in Figure 4) as observed experimentally (Figure 3).

Finally, it is interesting to consider the effect of nanogap conductivity on tip feedback current. In contrast to an insulating nanogap, a highly conductive nanogap can mediate a current that flows laterally through an unbiased nanoband to couple mediator regeneration under the tip with mediator electrolysis at the exterior surface of the nanoband. The resulting line scan over a nanoband with a highly conductive nanogap is expected to resemble a line scan over a gap-free nanoband and give a small or no peak current response to the gap. The current that flows laterally through an unbiased nanoband is approximated to the difference of currents at a tip above a nanoband and an insulating surface.^{12, 13} For instance, this current corresponds to ~ 6.3 and ~ 7.5 % of $i_{T,\infty} = 0.58$ nA at the gapped and gap-free nanobands, respectively, in Figure 3, thereby yielding a current density of 1.6 A/cm² with average cross section areas of 55 nm $\times$ 41 nm and 64 nm $\times$ 42 nm around the gap and center of the respective nanobands. This current density is comparable to a current density of > 0.88 A/cm² measured across an extremely narrow gap formed between a 85 nm-radius disk SECM probe with an intentionally unpolished, rough surface and an unbiased gold substrate.¹⁷ On the other hand, nanowire with one of the narrowest gaps reported so far is not conductive enough to affect a feedback tip current because a current density across the 2.5 nm-wide gap is only 1.5×10^{-4} A/cm² even with 1 V bias.⁶ Interestingly, the highest current density of 3.0×10^5 A/cm² with 1 V bias was obtained by filling a ~ 3 nm-wide gap with α,ω -dithiol terminated oligo(phenylene ethynylene), which serves as a conductive π -conjugated molecular wire that is nearly as long as the gap width.⁸ The magnitude of the current density varies with nanowires to be as low as only 0.1 A/cm² with 1 V bias, which was ascribed to different numbers of molecules that span a nanogap. The variations in the conductivity of the chemically modified nanogaps will be able to be probed by SECM with a conventional tip, where $w_g = 3$ nm and $2a = 1.2$ μ m correspond to $w_g/2a = 0.0025$ (see Figure 4).

CONCLUSIONS

This study demonstrates for the first time that a nanometer-scale gap in an unbiased nanowire can be detected and located by SECM with high sensitivity. The smallest gap that is detectable by SECM can be as small as 0.25 % of the tip diameter. The knowledge about a unique peak current response to a nanogap will be useful for spatially resolved SECM study of one-dimensional nanomaterials such as nanowires, nanotubes, and nanobands,^{12, 13} which may possess insulating nanogaps that are created intentionally or formed as defects. For instance, each pair of neighboring gaps in a nanowire with multiple nanogaps is resolvable by SECM if the fraction of the nanowire isolated between the adjacent gaps is long enough in comparison to the tip diameter to give a detectable feedback effect.¹³ Otherwise, the whole region of the isolated fraction and two adjacent nanogaps behaves as a single gap. Finally, SECM will also enable measurements of high conductivity of nanogaps when they are extremely narrow or bridged with conductive molecular wires for efficient electron transport.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Scheme of an SECM feedback experiment with a disk ultramicroelectrode probe positioned above a gapped nanowire on an insulating substrate.

Figure 2.
An SEM image of the 37 nm-wide gap in a 50 μm -long Au nanoband.

(a)

(b)

Figure 3. SECM line scans of 50 μm -long Au nanobands (a) with and (b) without a nanogap as obtained with a 2.0 μm -diameter disk Pt probe scanned at constant heights of 1.1 and 1.2 μm , respectively, from the nanoband surface. The scan rate was 3 $\mu\text{m/s}$.

Figure 4.

Simulated SECM line scans at the constant height of $d/a = 1$ from nanobands with a gap at $x = 0$. Solid lines represent line scans for gap sizes, $w_g/2a$, of 0.0025, 0.25, 1.0, and 2.5 from the top. Dotted lines correspond to line scans over a gap-free nanoband. All nanobands possess the same height, width, and length and mediate nernstian electron transfer.

Figure 5. Scheme of mediator regeneration and electrolysis at a gapped nanoband when a tip is positioned above the gap (top), and the center (middle) and edge (bottom) of a fragment.