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Scanning Electrochemical Microscopy of One-Dimensional Nanostructure: Effects of Nanostructure Dimensions on the Tip Feedback Current under Unbiased Conditions

Hui Xiong[†], Jiyeon Kim, Eunkyong Kim[‡], and Shigeru Amemiya^{*}

Department of Chemistry, University of Pittsburgh, 219 Parkman Avenue, Pittsburgh, Pennsylvania, 15260

Abstract

Scanning electrochemical microscopy (SECM) is developed as a powerful approach to electrochemical characterization of individual one-dimensional (1D) nanostructures under unbiased conditions. 1D nanostructures comprise high-aspect-ratio materials with both nanoscale and macroscale dimensions such as nanowires, nanotubes, nanobelts, and nanobands. Finite element simulations demonstrate that the feedback current at a disk-shaped ultramicroelectrode tip positioned above an unbiased nanoband, as prepared on an insulating substrate, is sensitive to finite dimensions of the band, i.e., micrometer length, nanometer width, and nanometer height from the insulating surface. The electron-transfer rate of a redox mediator at the nanoband surface depends not only on the intrinsic rate but also on the open-circuit potential of the nanoband, which is determined by the dimensions of the nanoband as well as the tip inner and outer radii, and tip–substrate distance. The theoretical predictions are confirmed experimentally by employing Au nanobands as fabricated on a SiO₂ surface by electron-beam lithography, thereby yielding well defined dimensions of 100 or 500 nm in width, 47 nm in height, and 50 μm in length. A 100 nm-wide nanoband can be detected by SECM imaging with ~2 μm-diameter tips although the tip feedback current is compromised by finite electron-transfer kinetics for Ru(NH₃)₆³⁺ at the nanoband surface.

Keywords

scanning electrochemical microscopy; feedback mode; one-dimensional nanostructure; gold nanoband; electron-beam lithography; finite element simulation

1. Introduction

Significant progress in synthesis and fabrication of one-dimensional (1D) nanostructures has been made over the past decade [1]. 1D nanostructures comprise anisotropic nanomaterials with both nanoscale and micro- to macro-scale dimensions, such as nanowires, nanotubes, nanobelts, and nanobands. A representative example is a carbon nanotube, which has been extensively studied since its report in 1991 [2]. More recently, various approaches have been

^{*}To whom correspondence should be addressed. amemiya@pitt.edu. Fax: 412-624-5259.

[†]Current address: School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138.

[‡]Current address: Center for Biosystems Research, University of Maryland Biotechnology Institute, College Park, MD 20742

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developed to prepare 1D nanomaterials with controlled shapes and dimensions from metals, semiconductors, and organic materials to manipulate their physical and chemical properties. On one hand, metallic and semi-conductive 1D nanostructures can be single crystals, where electronic transport is not governed by impurity or grain boundary scattering [3]. On the other hand, the composition of a 1D nanostructure can be altered along its long axis in a controlled manner [4].

Conductive and semi-conductive 1D nanostructures serve as novel electrode materials with fundamental and practical importance. Traditionally, such electrodes with both nanoscale and macroscale dimensions have been explored in electroanalytical chemistry [5] because of the unique mass transfer properties of the high-aspect-ratio electrodes [6-9]. The anisotropic nanoelectrodes give a large and easily measurable faradic current, which varies with the macroscopic dimension. Non-faradic current, which depends on the total surface area, is suppressed at the nanoelectrodes, thereby lowering a voltammetric detection limit as demonstrated by employing nanoband electrodes based on the exposed edge of a ultrathin metal film sandwiched between insulating layers [10] as well as carbon-nanotube-network electrodes [11]. A large local flux governed by the nanometer dimension allows for the study of nanoscale mass-transfer processes [12] and fast heterogeneous electron transfer (ET) kinetics [13]. Moreover, a larger interfacial capacity and the cathodic shift of the potential of zero charge were predicted theoretically for monoatomic nanowires, which differ from bulk electrodes in the double layer structure and work function [14]. Also, ET kinetics at a single-walled carbon nanotube was predicted to depend on the diameter and atomic structure of the tube, which control its electronic structure [15].

Recently [16], we proposed the “local” feedback mode of scanning electrochemical microscopy (SECM) [17,18] to quantitatively probe an ET process at individual 1D nanostructures as prepared or placed on an insulating surface. In this feedback mode, a disk-shaped ultramicroelectrode tip is positioned above a conductive 1D nanostructure to electrolyze redox mediator molecules at the tip (Figure 1). The tip-generated species reacts at the surface of the nanostructure directly under the tip to regenerate the original mediators. The mediator regeneration occurs without an external circuit connected to the nanostructure, which mediates efficient transport of electrons to (or from) the original mediators at the exterior surface exposed to the bulk solution. An open circuit potential of such an unbiased nanostructure can be large enough to drive the mediator regeneration to a diffusion limitation when the largest dimension of the nanostructure is much larger than the tip diameter. The large diffusion-limited flux of the regenerated mediators from the nanostructure surface to the tip significantly enhances the tip current. It was predicted theoretically that a nanoband with a width that is much smaller than the smallest SECM tips (≥ 30 nm in diameter [19]) is detectable in the local feedback mode even by employing a micrometer-sized tip when the diffusion limitation is achieved. On the other hand, the largest dimension of typical 1D nanostructures reported so far is finite in comparison to a micrometer-sized tip so that a diffusion-limited condition is not necessarily expected, thereby compromising the tip feedback current.

Here we investigate the tip feedback current with 1D nanostructures with finite dimensions by considering as models nanometer-wide bands with a micrometer length and a nanometer height. A numerical model developed for unbiased disk substrates [20] is extended to predict the dependence of tip feedback current on nanoband dimensions and finite ET kinetics as well as SECM geometries including tip inner and outer radii and tip-substrate distance. While a variety of unbiased substrates were studied experimentally by SECM [17,18], theories for the unbiased conditions were developed only for infinitely large substrates or finite disk-shaped substrates [20-22]. The theoretical predictions are assessed experimentally by investigating 50 μm -long Au nanobands with 100 or 500 nm in width and 47 nm in height as fabricated on the SiO_2 surface by electron-beam lithography. $\text{Ru}(\text{NH}_3)_6^{3+}$ is employed as a facile redox mediator

to find rather slow ET kinetics at the Au nanobands. We ascribe the slow ET rates to the passivation of the nanoband surface with Cr oxide that originates from the underlying Cr adhesion layer [23,24].

2. Theory

2.1. Model

A three-dimensional SECM diffusion problem with a finitely long nanoband positioned under a disk probe is defined in the Cartesian coordinate [16] (Figure 2). The origin of the coordinate axes is set at the center of the disk tip with the radius, a . A band electrode is placed on an insulating substrate in parallel to the probe surface such that the band center is just under the origin. The distance between the tip and band surfaces is given by d . The nanometer width and height, and micrometer length of the band are defined as w , h , and l , respectively. Actual simulations are carried out in the quarter of the whole domain with $x, y > 0$. The outer radius of the insulating substrate corresponds to $50a$ and limits the simulation space in the x and y directions. The simulation space behind the tip is defined by $20a$ to simulate the significant back diffusion of a mediator at a probe with small RG ($= r_g/a$) < 10 [25], where r_g is the outer radius of the insulating sheath at the tip. The overall simulation space is large enough for 3D simulations of the following SECM diffusion problem to give the largest errors of a few percents with an insulating substrate [16,26].

Amperometric tip current is based on a diffusion-limited reduction of O to R at the tip ($O + ne \rightarrow R$). Initially, the solution phase contains only one redox-active mediator, O. When the tip is positioned in the bulk solution, a steady-state diffusion-limited current at the tip, $i_{T,\infty}$, is given by

$$i_{T,\infty} = 4\pi nFDc_0a \quad (1)$$

where x is the function of RG [27], n is the number of electrons transferred per redox molecule, F is Faraday's constant, D and c_0 are the diffusion coefficient and concentration of the redox mediator in the bulk solution. On the other hand, the SECM diffusion problem was solved numerically to obtain the tip current, i_T , at the tip-substrate distance, d , as given by

$$i_T = 2\pi nFD \int_0^a x \left[\frac{\partial c}{\partial z} \right]_{y,z=0} dx \quad (2)$$

The solution of the diffusion problem with an unbiased nanoband was considered to be accurate when the potential of the nanoband, E , was chosen such that the substrate current, i_s , is less than 1% of $i_{T,\infty}$ to satisfy the zero-current condition at the unbiased nanoband [20]. The substrate current is given by

$$i_s = nFD \oint \left[\frac{\partial c}{\partial z} \right]_{z=d-h} dS \quad (3)$$

The nanoband is assumed to be conductive enough to maintain the uniform potential within the phase. The plots of the tip current and the corresponding open-circuit potential versus the

tip–substrate distance give current and potential approach curves, respectively (specifically at $d/a = 0.1, 0.15, 0.25, 0.4, 0.6, 0.8, 1, 1.25, 1.5, 1.75$, and 2 in this theory section).

2.2. Diffusion problem

A three-dimensional SECM diffusion problem is defined by

$$D \left[\frac{\partial^2 c(x, y, z)}{\partial x^2} + \frac{\partial^2 c(x, y, z)}{\partial y^2} + \frac{\partial^2 c(x, y, z)}{\partial z^2} \right] = 0 \quad (4)$$

where $c(x, y, z)$ is a steady-state concentration of O. A steady state was assumed in eq 4 although only a quasi-steady state is expected with a long nanoband (see 2.6). The diffusion coefficients of O and R are assumed to be the mean value so that mathematical treatment is restricted to the concentration of O.

A boundary condition on the nanoband surface depends on the rate of mediator regeneration. A substrate boundary condition for reversible mediator regeneration is given by Nernst equation as

$$E = E^{0'} - \frac{RT}{nF} \ln \frac{c_0 - c(x, y, d)}{c(x, y, d)} \quad |x| \leq l/2, y \leq w/2 \quad (5)$$

where $E^{0'}$ is the formal potential. When the mediator regeneration is kinetically limited, only one-step, one-electron transfer processes ($n = 1$) are considered

where $k_{\text{f},\text{s}}$ and $k_{\text{b},\text{s}}$ are the first-order heterogeneous rate constants. The rate constants are given by the Butler-Volmer relations as

$$k_{\text{f},\text{s}} = k^0 \exp[-\alpha F(E - E^{0'})/RT] \quad (7)$$

$$k_{\text{b},\text{s}} = k^0 \exp[(1 - \alpha)F(E - E^{0'})/RT] \quad (8)$$

where k^0 is the standard rate constant, and α is the transfer coefficient. The corresponding substrate surface boundary condition is given by

$$\begin{aligned}
 D \left[\frac{\partial c(x, y, z)}{\partial z} \right]_{z=d} &= -k_{f,s} c(x, y, d) + k_{b,s} [c_0 - c(x, y, d)] \quad |x| \leq l/2, y \leq w/2
 \end{aligned}
 \tag{9}$$

Moreover, diffusion-limited mediator regeneration, which is achieved at an unbiased infinitely long nanoband [16], is considered for a biased finitely long nanoband with $l/2a \leq 40$ (see sections 2.3 and 2.4). The corresponding boundary condition is given by

$$c(x, y, d) = c_0 \quad |x| \leq l/2, y \leq w/2 \tag{10}$$

The boundary condition at the tip surface is given by

$$c(x, y, 0) = 0 \quad x^2 + y^2 \leq a^2 \tag{11}$$

The other boundary conditions are given in Figure 2.

This steady state SECM diffusion problem was solved using COMSOL Multiphysics version 3.4 (COMSOL, Inc., Burlington, MA), which applies the finite element method. Calculation at each tip position took < 2 min on a PC equipped with an Intel Core2 Quad CPU at 2.4 GHz and 4.0 GB RAM with Windows XP Professional. With the large space required for incorporating long nanobands ($l/2a \leq 40$), the band width that allows for successful simulations by this software under given conditions was technically limited to $w/2a \geq 0.015$. This theory section is focused on $w/2a = 0.015$ while wider bands are studied experimentally in Results and discussion, where the tip current increases monotonically as the band becomes wider. Unfortunately, the limited widths are too large to observe the logarithmic dependence of the tip current on the band width, i.e., a negative local feedback effect, which enables SECM detection of extremely narrow band [16].

2.3. Diffusion-limited feedback at biased inlaid nanobands with various lengths

SECM approach curves were simulated for nanobands with various lengths under a diffusion-limited condition at the nanoband surface (eq 5). The application of an external bias to a finitely long nanoband ($l/2a \leq 40$) is required for diffusion-limited mediator regeneration (see 2.4). A very short nanoband is detectable under the diffusion-limited condition, where mediator regeneration is most efficient to maximize the tip feedback current. Moreover, mediator regeneration at the biased nanoband is coupled with electron transport to an external circuit, thereby eliminating the need of an exterior nanoband surface for electrolysis of the original mediators (Figure 1). The approach curve simulated under the diffusion-limited condition becomes only slightly negative as $l/2a$ decreases from 40 to 1.5 (the top dotted and solid lines, respectively, in Figure 3a), which is long enough to efficiently collect the tip-generated species for mediator regeneration. As a band becomes shorter than $l/2a = 1.5$, an approach curve becomes more negative. A nanoband with $l/2a = 0.1$, however, is still distinguishable from an insulating surface.

The simulation results demonstrate that a nanoband with a very small surface area is detectable by SECM under the diffusion-limited condition. Bands with $w/2a = 0.015$ and $l/2a = 0.1$ –1.5

possesses total surface areas of only 0.0048–0.072 % with respect to the tip area. In contrast, SECM allows for the identification of a biased disk substrate with the radius that is at least 10 % of the tip radius, corresponding to a total substrate area of >1 % with respect to the tip area [28]. A nanoband with a much smaller area is detectable, because the local feedback effect weakly depends on the width of a band when the width is much narrower than the tip diameter ($w \ll 2a$) [16].

2.4. Reversible feedback at unbiased inlaid nanobands with various lengths

Effects of band length on the tip current were examined for reversible ET at unbiased nanobands as defined by the Nernst equation (eq 6). In comparison to the biased, diffusion-limited case, a much longer nanoband is required for SECM detection under an unbiased condition. The large exterior surface of an unbiased nanoband must be exposed to the bulk solution for mediator electrolysis, which is coupled with mediator regeneration at the nanoband surface under the tip (Figure 1). Simulated approach curves demonstrate that an unbiased nanoband with $l/2a = 40$ (the top solid line in Figure 3b) is not long enough to drive mediator regeneration to a diffusion limitation (the top dotted line in Figure 3b). An approach curve becomes more negative with a shorter nanoband in the range of $5 < l/2a < 40$. An approach curve is very negative with a nanoband with $l/2a = 5$, which is ~ 50 times longer than the shortest nanoband that is detectable by SECM under a diffusion-limited condition.

A shorter nanoband under an unbiased condition possesses a smaller overpotential for mediator regeneration as given by $E - E^{0'}$ (the inset of Figure 3b), thereby yielding a smaller tip feedback current. The open circuit potential of an unbiased nanoband is set such that the total influx of electrons into the nanoband by mediator regeneration (or electrolysis) balances with the total efflux of electrons from the nanoband by mediator electrolysis (or regeneration). A nanoband with $l/2a > 1$ is long enough to efficiently collect the tip-generated species at short tip–substrate distances. The smaller exterior surface of a shorter nanoband, however, is exposed to the bulk solution for mediator electrolysis, thereby resulting in a smaller overpotential for mediator regeneration.

Notably, an unbiased nanoband with a much smaller area is detectable by SECM in comparison to an unbiased disk. Only ~ 1 % of the substrate surface just under a tip is covered by a nanoband with $w/2a = 0.015$. In contrast, an unbiased disk substrate must be larger than the disk tip for detecting a feedback effect, thereby corresponding to a relative substrate area of >100 % [20]. The larger feedback effect at an unbiased nanoband is ascribed to weak width dependence of the flux based on hemicylindrical diffusion of the original and tip-generated redox species at the nanoband [16]. Moreover, a substrate with a higher aspect ratio exposes a larger exterior surface to the bulk solution for mediator electrolysis.

2.5. Tip current dependence on band height

The finite element simulation also demonstrates that the tip feedback current is larger with a higher nanoband, which possesses a larger surface area that is available for both regeneration and electrolysis of a redox mediator. The feedback effect is more enhanced for diffusion-limited ET than for reversible ET when $h/2w$ varies from 0 to 2 (the top dotted and dashed lines, respectively, in both Figure 3a and b). The enhanced feedback effect is remarkable at short tip–substrate distances, where the tip current becomes more positive with a higher nanoband. A hemicylindrical diffusion layer at a higher nanoband interacts more significantly with the tip surface positioned at a short distance from the insulating substrate surface (Figure 4a) so that the resulting thinner diffusion layer at a higher nanoband gives a more positive current change. Significant effects of the band height on kinetically limited feedback current are also demonstrated experimentally (see 4.2 and 4.3).

2.6. Quasi-steady-state diffusion at unbiased nanobands

Steady-state diffusion without a convection effect as assumed in our model is a good approximation for quasi-steady-state hemicylindrical diffusion at a long nanoband [6-9] under the SECM configuration. The hemicylindrical diffusion layer with the thickness that is controlled by the band width and height is developed not only at the region of the nanoband surface under the tip (Figure 4a) but also at the region exposed to the bulk solution (Figures 4b). A mediator concentration at the exposed surface, however, recovers quickly from 86 % of the bulk concentration to 92 % within the small region depicted in Figure 4b and then gradually to 99 % at 15 normalized distances from the surface. This concentration profile is only slightly affected by the simulation space limits. This result predicts that a quasi-steady-state concentration profile is maintained at long times without a convection effect, which is significant in the outside of the 99% contour with a micrometer-sized tip. A true steady state at a long nanoband under an SECM probe requires biased conditions, where no mediator electrolysis at the long exposed surface occurs.

2.7. Kinetically limited feedback current

The SECM tip current depends on heterogeneous ET kinetics at an unbiased nanoband with a finite length, which is not long enough to drive mediator regeneration to a diffusion limitation. Here we employ inlaid nanobands to evaluate this kinetic effect, which is also addressed experimentally for raised nanobands (see 4.2 and 4.3). Simulations were carried out for unbiased inlaid nanobands with $w/2a = 0.015$ and $l/2a = 40$ to investigate the kinetic effect for quasi-reversible ET as defined by Butler-Volmer relations [29] (eqs 8 and 9). An intrinsic ET rate in the simulations was defined in the normalized form, K , as given by

$$K = \frac{k^0 a}{D} \quad (12)$$

As K becomes smaller from 100 to 1, the corresponding approach curve becomes more negative to change from a reversible curve to a purely negative curve despite the large overpotential of the relatively long nanoband with $l/2a = 40$ (the inset of Figure 5). A similar trend was also observed with a shorter unbiased nanoband with $l/2a = 12$ (data not shown).

It should be noted that a reversible response at an unbiased nanoband requires $K > 100$, which is much larger than the K value of ~ 10 required for a reversible response at an unbiased disk substrate [20]. A K value represents the ratio of a k^0 value with respect to a steady-state mass transfer coefficient at the tip in a bulk solution, i.e., $\sim D/a$, which increases to $\sim D/d$ with a large conductive substrate under the tip ($d < a$) [30]. These mass transfer coefficients, however, are much smaller than the corresponding steady-state mass transfer coefficient at a nanoband under an SECM tip. The mass transfer coefficient based on hemicylindrical diffusion at the nanoband is inversely proportional to the band width and logarithmically depends on the tip-substrate distance and tip diameter when the band width is much smaller than the tip diameter ($w \ll 2a$) [16]. The faster mass transfer at a nanoband results in a kinetic limitation with a larger K value.

2.8. Effects of tip RG under reversible conditions

The feedback mechanism with an unbiased nanoband is better understood by considering effects of tip RG on the tip feedback current. With a thinner insulating sheath surrounding the tip, a larger exterior surface of a nanoband is exposed to the bulk solution for electrolysis of original mediator molecules (Figure 1). More efficient mediator electrolysis enhances mediator regeneration at the nanoband surface under the tip, thereby resulting in a larger tip current. The

RG effects were simulated for reversible ET at an inlaid nanoband with $l/2a = 10$ (Figure 6a). The simulation results confirm a larger current at a tip with a smaller outer radius in the range of $1.5 \leq RG \leq 20$. Moreover, the approach curve with $RG = 1.5$ is much steeper at short distances in comparison with the curves with $RG = 4$ and 7. The RG dependence of approach curves is similar to that with a purely insulating substrate [25], indicating that this result is due to much less hindered diffusion of redox molecules from the bulk solution to the tip with $RG = 1.5$. The simulated fluxes of the original mediators at the nanoband surface support the mechanism of the RG effect (Figure 6b). A negative flux based on mediator regeneration is localized under the tip with any RG, indicating that a nanoband with $l/2a > 1$ is long enough to efficiently collect tip-generated species. A larger negative flux under a tip with smaller RG is balanced by a larger positive flux based on mediator electrolysis, which occurs at a larger exposed surface of the nanoband in the region of $\sim RG < x/a \leq 10$. Overall, the tip feedback current depends on the band length with respect to the tip outer diameter, i.e., $l/2r_g$.

The RG effect at an unbiased nanoband is moderate in comparison to that at an unbiased disk substrate, which gives a positive approach curve when the tip outer diameter is comparable to or smaller than the substrate diameter [20]. In contrast, a negative approach curve at an unbiased nanoband is limited by the band width when the tip outer diameter is much smaller than the band length, i.e., $w \ll 2r_g \ll l$, thereby achieving diffusion-limited conditions [16]. Moreover, an overpotential at the unbiased nanoband with $w/2a = 0.015$ and $l/2a = 10$ becomes larger with smaller RG but is not large enough to drive the mediator regeneration to the diffusion limitation even with $RG = 1.5$ (the inset of Figure 6a). In fact, the significant fraction of the large tip current with $RG = 1.5$ is ascribed to less hindered diffusion of redox mediator molecules from the bulk solution to the tip [31].

3. Experimental section

3.1. Nanoband fabrication by electron-beam lithography

An array of nanobands with 100 or 500 nm in width, 47 nm in height, and 50 μm in length was fabricated on a SiO_2 -covered silicon wafer by electron-beam lithography (Scheme 1). A 700 nm-thick thermal oxide was grown at 1100 $^\circ\text{C}$ under flowing O_2 on an RCA standard cleaned silicon chip (a 380 μm thick wafer polished on both sides, Silicon Quest, Santa Clara, CA). A side of the chip was spin-coated with poly(methylmethacrylate)/poly(methylmethacrylate-co-methacrylic acid) as an electron-beam bilayer resist. An electron-beam tool (model EBPB-5HR, Leica Microsystems, Wetzlar, Germany) was used to expose the resist-coated chip to an electron beam. The exposed parts were dissolved by immersing the sample in the methyl isobutyl ketone:isopropyl alcohol (1:1 v/v) developer. A 5 nm-thick Cr film and then a 47 nm-thick Au film were deposited by electron-gun evaporation (Semicore Equipment, Inc., Livermore, CA, USA). The remaining resist and the metal on top of it were removed using Microposit Remover 1165. The lateral dimensions of the nanobands were characterized by field-emission SEM (model XL-30, Philips Electron Optics, Eindhoven, Netherlands) while the band height was determined by AFM (Dimension 3100, Digital Instrument, Inc., Santa Barbara, CA, USA) in tapping mode.

3.2. SECM measurements

A commercial SECM instrument with close-loop piezoelectric motors (CHI 910B, CH Instruments, Austin, TX, USA) was used for approach curve and imaging experiments. The instrument was placed on a vibration isolation platform (model 63-533, TMC, Peabody, MA, USA). A two-electrode setup was employed with a 1 mm-diameter AgCl-coated Ag wire (or a Ag wire for experiments with KClO_4 as supporting electrolytes) serving as a reference/counter electrode and a 2.2 or 2.8 μm -diameter Pt disk electrode with $RG = 10$ (CH Instruments) as an SECM probe. The inner and outer tip radii of the Pt probes were determined from current

approach curves at an insulating Teflon substrate [25,32]. The tip radii were also checked by optical microscopy.

The surfaces of the Au nanobands were cleaned before SECM experiments. Specifically, the nanoband array was soaked in acetone for 1 hour, dried with nitrogen, treated for 1 hour in a UV/ozone cleaner [33] (UV-tip Cleaner, BioForce Nanosciences, Ames, IA, USA), soaked in ethanol for 1 hour, and dried with nitrogen. The pretreatment did not change a dimension of a nanoband as confirmed by SEM and AFM.

The nanoband array was placed in an SECM cell filled with 0.1 or 0.05 M KCl containing 1 or 2 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ (Strem Chemicals, Newburyport, MA, USA) or 0.05 M KClO_4 containing $\text{Ru}(\text{NH}_3)_6(\text{ClO}_4)_3$. The perchlorate salt was prepared as a precipitate from the saturated aqueous solution of $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ by adding concentrated HClO_4 . The precipitate was filtered, washed with concentrated HClO_4 , and recrystallized from 0.05M HClO_4 at 0 °C. The purified salt is free from chloride, because no precipitate was detected after the addition of excess AgNO_3 to the aqueous solution of the salt. The aqueous solutions were prepared with 18.3 M Ω -cm deionized water (Nanopure, Barnstead, Dubuque, IA).

An SECM probe was positioned above the center of a nanoband for approach curve measurements. First, the probe was brought vertically to a short distance from the SiO_2 surface by monitoring a decrease of the tip current. Then, the tip center was positioned just above the nanoband during a line scan at a constant height in the y -direction, where a peak current was obtained (see 4.1). Finally, the tip was scanned laterally in the x -direction to find the center of the nanoband. SECM approach curves thus obtained were independent of a rate of the probe scan in the z -direction. The apparently steady-state approach curves were analyzed numerically by assuming steady-state diffusion of redox molecules without a convection effect (see 2.6). For imaging experiments, the tilt of a substrate was adjusted such that a nearly constant tip current is obtained during lateral scans.

4. Results and discussion

4.1 SECM imaging of a 100 nm-wide band

Here we apply SECM to electrochemical characterization of Au nanobands with finite dimensions as models of 1D nanostructures. The 50 μm length and 100 nm width of a Au nanoband as prepared on a SiO_2 -covered Si wafer by electron-beam lithography are confirmed by SEM images in Figures 7a and b. The height of the center of a nanoband from the surrounding SiO_2 surface is 47 ± 4 nm as determined by AFM. Such a Au nanoband enables us to investigate the dependence of the tip feedback current on the finite dimensions as well as finite ET kinetics, which were not addressable in our previous study of centimeter-long inlaid nanobands under diffusion-limited conditions [16].

An SECM image of a 100 nm-wide Au nanoband was obtained by scanning a 2.2 μm -diameter Pt disk probe with $\text{RG} = 10$ at a constant height (Figure 8a). The tip current based on $\text{Ru}(\text{NH}_3)_6^{3+}$ reduction increased above the nanoband during the lateral probe scan. This result indicates that $\text{Ru}(\text{NH}_3)_6^{2+}$ generated at the tip was oxidized at the nanoband surface to regenerate $\text{Ru}(\text{NH}_3)_6^{3+}$, which enhanced the tip current. The feedback effect is substantial although only 5.8 % of the substrate surface directly under the tip is covered with the nanoband. Moreover, the tip current at the periphery of the image is consistent with the negative feedback current as expected for the insulating SiO_2 surface under the tip. This result indicates that an adjacent nanoband, which was fabricated at least 200 μm far from the imaged nanoband, does not affect the tip current in the image.

The nanoband appears much wider than 100 nm in the image, where a spatial resolution is determined by the tip size. The spatial resolution is high enough to confirm a band length of 50 μm in the image. The variation of the tip current above the nanoband along the x -axis is partially due to heterogeneous reactivity or morphology of the nanoband surface. More importantly, representative cross sections of the image at $x = 12, 30$, and $48 \mu\text{m}$ (Figure 8b) demonstrate that the variation of the tip current is much smaller above the nanoband than above the surrounding SiO_2 surface. The gradual decrease of the tip current above the SiO_2 surface along the x -axis corresponds to the decrease of the tip–substrate distance caused by the tilt of the substrate surface. The substrate tilt results in a sharper peak current in the y -direction, because the tip feedback current depends on the distance more weakly above the nanoband than above the insulating surface (see 4.2).

4.2. Approach curve measurement with a 100 nm-wide band

A small feedback effect above the nanoband in the SECM image indicates that the 50 μm -long nanoband, which is 18 times longer than the tip diameter, is not long enough to drive $\text{Ru}(\text{NH}_3)_6^{3+}$ regeneration at the band surface to a diffusion limitation. The kinetic limitation is quantitatively demonstrated by studying current approach curves, where the tip current, i_T , was measured as a function of the tip–substrate distance, d . An approach curve at a 100 nm-wide band as measured with a 2.8 μm -diameter Pt disk probe with $\text{RG} = 10$ was plotted in the normalized form for numerical analysis (solid line in Figure 9). The tip current decreased monotonically as the tip center was brought vertically toward the band center. The approach curve at the nanoband, however, is less negative than that at the insulating SiO_2 surface (dotted line), confirming mediator regeneration at the nanoband surface. The approach curve at the nanoband is more negative than the curves simulated for diffusion-limited or reversible mediator regeneration at the nanoband with 47 nm in height. This result indicates that the mediator regeneration is kinetically limited at the nanoband. In fact, the experimental approach curve at the nanoband fits well with the quasi-reversible approach curve simulated for the raised nanoband with $K = 3.5$ and $\alpha = 0.5$. The theoretical curve strongly depends on K but not on α , because the overpotential for the mediator regeneration at the nanoband, $E - E^0$, is small during the tip approach (the inset of Figure 9) [20]. A larger K value of 17 as obtained by assuming an inlaid nanoband in the simulation is overestimated. This result confirms a significant effect of band height on the tip feedback current for a quasi-reversible substrate reaction.

It should be noted that electronic conduction in the unbiased Au nanoband is not the rate-determining step in the SECM feedback process although lateral electron transport through the nanoband is required for coupling mediator regeneration at the nanoband surface under the tip with mediator electrolysis at the exterior surface (Figure 1). A normalized approach curve with a 100 nm-wide Au band was identical at 1 and 2 mM mediator concentrations (data not shown), where the current flow through the nanoband varies. The concentration-independent feedback effect confirms a negligibly small potential drop in the conductive substrate [34]. This result justifies a uniform open circuit potential of a nanoband as assumed in our model to obtain theoretical approach curves that fit very well with experimental curves. Moreover, the negligible potential drop can be explained as follows. Au nanobands are more resistive than bulk Au materials because of a smaller cross-section area (100 or 500 nm $\times$ 47 nm for nanobands in this study) and a higher resistivity (6–30 $\mu\Omega\cdot\text{cm}$ for Au nanobands with similar nanoscale dimensions and $\sim 2 \mu\Omega\cdot\text{cm}$ for bulk Au materials [35,36]). Current that flows laterally through a nanoband in the SECM experiments, however, is as small as approximated to the difference of currents at a tip above the nanoband and insulating surfaces [16]. Overall, a flow of sub-nA current along the 50 μm -long Au nanobands with a $\sim \text{k}\Omega$ resistance results in only a $\sim \mu\text{V}$ potential drop in the nanoband.

4.3. Approach curve measurement with a 500 nm-wide band

A 50 μm -long band with 500 nm in width and 47 nm in height was also studied to assess effects of the band width and height on the tip feedback current. An approach curve with the 500 nm-wide band (solid line in Figure 10) is more positive than that with the 100 nm-wide band. Moreover, the tip current with the 500 nm-wide band depends more weakly on the band height. A K value of 3.5 is obtained from a good fit with an approach curve simulated with 47 nm in height while a K value of 6 was obtained with an assumption of an inlaid nanoband in the simulation. This result with the 500 nm-wide band contrasts to that with the 100 nm-wide band, where a change of the height from 47 to 0 nm in simulations changed K from 3.5 to 17, indicating that the neglect of the band height causes more significant overestimation of the K value at the narrower nanoband.

The K value of 3.5 as obtained with the 100 and 500-nm wide raised nanobands correspond to $k^0 = 0.19 \text{ cm/s}$ in eq 4 with the given tip radii and a diffusion coefficient of $7.5 \times 10^{-6} \text{ cm}^2/\text{s}$ for $\text{Ru}(\text{NH}_3)_6^{3+}$ in the aqueous electrolyte solutions. These k^0 values are significantly smaller than those of the same redox couple at Au electrodes in 0.1 M HClO_4 (1.43 cm/s [37]), 1.0 M KF (1.0 cm/s [38,39], and 1.7 cm/s [40]), and 1 M H_2SO_4 (0.85–5.5 cm/s [41]). The smaller k^0 values are not due to a double layer effect based on strong adsorption of Cl^- on the Au surface [42] because a similar k^0 value was obtained by using weakly adsorbing ClO_4^- as an electrolyte, i.e., in 0.05 M KClO_4 containing 1 mM $\text{Ru}(\text{NH}_3)_6(\text{ClO}_4)_3$ (data not shown). Moreover, Mirkin and co-workers reported much larger k^0 values of 13.5 and 9.3 cm/s for this redox couple in 0.5 M KCl and 1 M KF , respectively, by using SECM with a nanometer-sized Au probe [43]. We ascribe the smaller k^0 values to the passivation of the Au nanoband surface with Cr oxide, which is formed at the surface by rapid diffusion of Cr from the adhesion layer through the thin Au layer [23,24]. The passive Cr oxide slows down the kinetics of $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ couple as observed with oxide-covered Cr electrodes, where k^0 decreases from 0.36 to 0.00025 cm/s in 1 M H_2SO_4 as the thickness of the oxide layer increases from 0.5 to 2 nm [41].

5. Conclusions

This work extends the applicability of SECM to electrochemical characterization of 1D nanostructures with finite dimensions. Moreover, SECM measurements under unbiased conditions eliminate the integration of the nanostructures into the electrode format by the multiple lithographic processes, which is required for conventional voltammetric characterization [13,44]. At the same time, finite ET kinetics at an unbiased 1D nanostructure with finite dimensions compromises the tip feedback current in comparison to a diffusion-limited or a reversible case, thereby requiring a probe that is much smaller than the largest dimension of a 1D nanostructure.

High sensitivity of SECM to dimensions of 1D nanostructures was demonstrated both theoretically and experimentally. A good agreement between simulated and experimental approach curves confirms the well-defined dimensions of the nanobands as fabricated by electron-beam lithography. With the knowledge of the dimensions, the redox activity of individual 1D nanostructures was probed by SECM, thereby revealing rather slow ET kinetics for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ couple at the Au nanobands with a Cr adhesion layer.

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Figure 1.
Scheme of an SECM feedback experiment with a disk ultramicroelectrode probe above a conductive 1D nanostructure (nanoband) on an insulating substrate.

Figure 2.

Geometry of the SECM diffusion problem in the Cartesian coordinate as represented by cross sections at $y = 0$ (left) and $x = 0$ (right). There is no normal flux at dashed lines while dash-dot lines represent simulation space limits.

Figure 3a

Figure 3b

Figure 3.

Effects of band length and height on steady-state current approach curves for (a) diffusion-limited ET at a biased nanoband and (b) reversible ET at an unbiased nanoband as simulated for a disk probe with $RG = 10$. For both inlaid nanobands, $h = 0$ and $w/2a = 0.015$. The solid lines are for inlaid nanobands with $l/2a =$ (a) 1.5, 1, 0.75, 0.5, 0.25, 0.1 and (b) 40, 15, 12, 10, 5 from the top. The dashed lines are for raised nanobands with $l/2a = 40$ and $h/w = 2$ and 1 from the top. The upper dotted lines represent a diffusion-limited curve at a nanoband with $w/2a = 0.015$ and $l/2a = 40$. The lower dotted lines represent an approach curve at an insulating substrate. The inset in (b) shows corresponding potential approach curves at the inlaid nanobands with $l/2a = 40, 15, 12, 10, 5$ from the top.

Figure 4.

Simulated concentration profiles of a reversible redox mediator at $x =$ (left) 0 and (right) 20 simulated for an unbiased raised nanoband with $w/2a = 0.015$, $l/2a = 40$, and $h/w = 2$. The distance between the tip and insulating substrate is $0.1a$. The tip RG is 10. The mediator concentration at the nanoband surface is $0.86c_0$.

Figure 5.

Effects of ET kinetics on steady-state current approach curves at an unbiased inlaid nanoband with $w/2a = 0.015$ and $l/2a = 40$ as simulated for a disk probe with $RG = 10$. The solid lines are for $K = 100, 25, 10, 5, 2.5, 1$ from the top. The upper dotted line represents a reversible curve at the nanoband. The lower dotted line represents an approach curve at an insulating substrate. The solid lines in the inset represent corresponding potential approach curves for $K = 100, 25, 10, 5, 2.5, 1$ from the bottom, where curves for $K = 5, 2.5, 1$ overlap. The dotted line is a reversible curve.

Figure 6a

Figure 6b

Figure 6.

(a) RG effects on reversible approach curves at an unbiased inlaid nanoband with $w/2a = 0.015$ and $l/2a = 10$ as simulated at a steady state for disk probes with $RG = 1.5, 4, 7, 10, 20$ from the top (solid lines). The upper dotted line represents a diffusion-limited curve at the nanoband for the probe with $RG = 1.5$. The lower dotted line represents an approach curve at an insulating substrate for the probe with $RG = 20$. The inset shows corresponding potential approach curves for probes with $RG = 1.5, 4, 7, 10, 20$ from the top. (b) Simulated steady-state fluxes at the surface of the nanoband along the x -axis at $y = 0$ and $z = d = 0.1a$ for probes with $RG = 1.5, 7$, and 10 (dotted, solid, and dashed lines, respectively).

Figure 7. Lower (left) and higher (right) resolution SEM images of a Au nanoband with 100 nm in width, 50 μm in length, and 47 nm in height as fabricated on a SiO₂/Si surface by electron-beam lithography.

Figure 8a **Figure 8b** **Figure 8.**

(a) An SECM image of a 100 nm-wide Au band as obtained using a 2.2 μm -diameter disk Pt probe with $\text{RG} = 10$ at a constant height. The scan rate was 15 $\mu\text{m}/\text{s}$. The nanoband was

immersed in 0.1 M KCl containing 1 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$. (b) SECM line scans at $x = 12, 30$, and $48\text{ }\mu\text{m}$ in the image (solid, dashed, and dotted lines, respectively).

Figure 9.

Normalized approach curves at a 100 nm-wide Au band (solid line) and a SiO_2 surface (dotted line) as obtained using a 2.8 μm -diameter disk Pt probe with $\text{RG} = 10$ in 0.1 M KCl containing 1 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$. The scan rate was 0.75 $\mu\text{m/s}$. The symbols represent the curves simulated for quasi-reversible (circles; $K = 3.5$), reversible (crosses) and diffusion-limited (diamonds) ET at a raised nanoband with $w/2a = 0.036$, $h/2a = 0.017$, and $l/2a = 18$. The triangles represent a purely negative approach curve at an insulating surface. The inset show corresponding potential approach curves for the quasi-reversible (circles) and reversible (crosses) cases.

Figure 10.

Normalized approach curves at a 500 nm-wide Au band (solid line) and a SiO_2 surface (dotted line) as obtained using a 2.8 μm -diameter disk Pt probe with $\text{RG} = 10$ in 0.1 M KCl containing 1 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$. The scan rate was 0.75 $\mu\text{m/s}$. The symbols represent the simulated curves as defined in the caption of Figure 9 at a raised nanoband with $w/2a = 0.18$, $h/2a = 0.017$, and $l/2a = 18$, or the insulating surface. The circles represent a quasi-reversible response with $K = 3.5$.

Scheme 1.
Nanoband Fabrication