Supporting Information

Local Feedback Mode of Scanning Electrochemical Microscopy for Electrochemical Characterization of One-Dimensional Nanostructure: Theory and Experiment with Nanoband Electrode as Model Substrate

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Nanoband electrodes were characterized using cyclic voltammetry (Figure S1). The forward and reverse sweep voltammograms overlap and give slightly peak-shaped waves. The voltammograms fit well with a theoretical diffusion-limited voltammogram given by[1]

$$i = \frac{nFc_0 Dl[0.97 - 0.11\exp\{-9.9/\ln(5(\xi+1)p^{-2})\}]}{1+\exp(-\xi)} \quad \text{(S1)}$$

with

$$p = (nFvw^2/RTD)^{1/2} \quad \text{(S2)}$$

$$\xi = (nF/RT)(E - E^{0'}) \quad \text{(S3)}$$

where v is the potential sweep rate and $E^{0'}$ is the formal potential. With $D = 8 \times 10^{-6}$ cm^2/s, w = 100 nm, and v = 0.010 V/s, the band length of 2.6 cm was obtained, which agree with the physical length, confirming that the redox reaction at the narrow band surface is diffusion-limited.

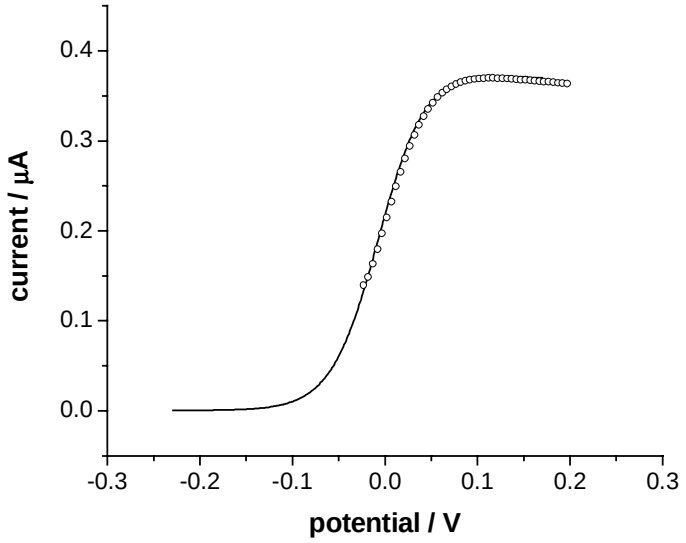

Figure S1. Cyclic voltammograms at a nanoband electrode in 5 mM $Ru(NH_3)_6Cl_3$ with 0.1 M KCl. The solid line is an experimental response and the circles were obtained using eq S1.

In line scan experiments with a 25 μm-diameter Pt disk probe (RG = 10), ascorbic acid was used as an irreversible redox molecule, which gives a negative feedback effect both at conductive and insulating substrates. The tip current based on oxidation of ascorbic acid at the 25 μm-diameter decreases as the tip is brought to a 2 mm-diameter Pt substrate (Figure S2), resulting in an approach curve that fits with a theoretical curve with an insulating substrate. This result is not due to fouling of the Pt substrate surface by products of the oxidation reaction, where a positive feedback effect was observed using $Ru(NH_3)_6^{3+}$ as a reversible mediator. Similarly, positive and negative feedback effects were observed at the Pt substrate using a 10 μm-diameter Pt disk probe with the respective redox molecules.

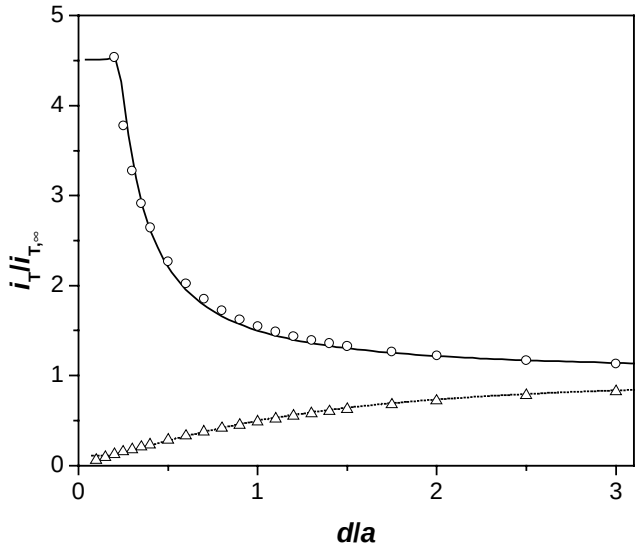

Figure S2. SECM approach curves at a 2 mm-diameter Pt substrate obtained using a 25 μm-diameter Pt disk probe with $Ru(NH_3)_6^{3+}$ (solid line) and ascorbic acid (dotted line) as a redox-active molecule in their mixed solution. The circles and triangles represent theoretical approach curves with a conductor and an insulator, respectively.

REFERENCES

(1) Aoki, K.; Tokuda, K. *J. Electoanal. Chem.* **1987**, *237*, 163-170.