Supporting Information

Fluorinated Xerogel-Derived Ultramicroelectrodes for Amperometric Nitric Oxide Sensing

*Jae Ho Shin, Benjamin J. Privett, Justin M. Kita, R. Mark Wightman, and Mark H. Schoenfisch**

Contribution from the Department of Chemistry, University of North Carolina at Chapel Hill,
Chapel Hill, North Carolina 27599

* To whom correspondence should be addressed. E-mail: schoenfisch@unc.edu

1. Electrooxidation process of nitric oxide on a platinum working electrode.

The electrochemical oxidation of NO on a polycrystalline platinum electrode proceeds via the following reactions.[S1-S3] In the first step (Eq. S1) an electron is transferred from NO to the electrode, generating an oxidation current. Since nitrosonium ion (NO^+) is a relatively strong Lewis acid, it is converted to nitrite (NO_2^-) in the presence of hydroxide (OH^-) (Eq. S2).

$$NO \rightarrow NO^+ + e^- \tag{S1}$$

$$NO^+ + OH^- \rightarrow HNO_2 \tag{S2}$$

Ultimately NO_2^- is further oxidized to nitrate (NO_3^-), the final product of NO's electrochemical oxidation, resulting in the additional transfer of two electrons to the platinum electrode:

$$HNO_2 + H_2O \rightarrow NO_3^- + 3H^+ + 2e^- \tag{S3}$$

2. Calculation of the concentration for a standard NO solution (adapted from ref. S4).

The molarity of NO (C_{NO}, mol·L^{-1}) in phosphate-buffered saline (PBS; containing 3.9 mM NaH_2PO_4, 6.1 mM Na_2HPO_4, 2.7 mM KCl, and 138 mM NaCl) can be calculated from Henry's law:

$$C_{NO} = P_{NO}S_{NO} \tag{S4}$$

where P_{NO} is the pressure of NO (mmHg), and S_{NO} is the solubility of NO in water (cm^3). Alternatively, C_{NO} and S_{NO} in water may be calculated as C_{NO} and S_{NO} in saline or PBS. The pressure of NO (P_{NO}) may be expressed as follows.

$$P_{NO} = (P_{tot} - P_w)(G_{NO})10^{-6} \tag{S5}$$

where P_{tot} and P_w are the total pressure (760 mmHg) of the gas mixture and the partial pressure of water vapor (23.8 mmHg)[S5] at 25 °C, respectively. In addition, G_{NO} is the NO concentration obtained from a gas cylinder (ppm). For our studies, S_{NO} at 25 °C is 0.0432 cm^3.[S6] Finally, converting the units of pressure from mmHg to mol·L^{-1} yields the following expression:

$$C_{NO} = (760 - 23.8)\frac{133.322 \times 10^{-3}}{8.314(273.15 + 25)}(G_{NO})10^{-6}(0.0432) \tag{S6}$$

Therefore, when PBS is purged with 24.1 ppm of NO gas (G_{NO}), C_{NO} is about 41 nM.

Table S1. Electrochemical characteristics of fluorinated xerogel-derived NO sensors as a function of xerogel composition[a]

Xerogel composition[b,c]	Permeability, P_i^e		Permselectivity, α_{NO,NO_2^-}	Selectivity,[d] $\log K^{amp}_{NO,NO_2^-}$
	i = NO	i = NO_2^-		
Bare Pt (blank)				–1.51 ± 0.09
MTMOS (control)	0.52 ± 0.05	0.32 ± 0.09	1.6 ± 0.5	–1.74 ± 0.16
BTMOS (control)	0.83 ± 0.08	0.83 ± 0.12	1.0 ± 0.2	–1.60 ± 0.03
20% 3FTMS/MTMOS	0.77 ± 0.11	0.19 ± 0.04	4.1 ± 1.0	–2.00 ± 0.20
20% 9FTMS/MTMOS	0.20 ± 0.09	0.061 ± 0.009	3.3 ± 1.6	–1.90 ± 0.10
20% 13FTMS/MTMOS	0.51 ± 0.08	0.053 ± 0.007	10 ± 2	–2.22 ± 0.11
20% 17FTMS/MTMOS	0.75 ± 0.06	0.0091 ± 0.001	83 ± 11	–3.21 ± 0.15
20% 17FTMS/MTMOS/HCl	0.72 ± 0.09	<0.0001	7200 ± 900	–5.74 ± 0.14
20% 17FTMS/MTMOS/NaOH	0.13 ± 0.02	<0.0001	1300 ± 200	–4.83 ± 0.09
10% 17FTMS/MTMOS/HCl	0.92 ± 0.05	0.047 ± 0.009	20 ± 4	–3.11 ± 0.21
30% 17FTMS/MTMOS/HCl	0.33 ± 0.03	<0.0001	3300 ± 300	–5.10 ± 0.14
40% 17FTMS/MTMOS/HCl	0.11 ± 0.05	<0.0001	1100 ± 500	–4.57 ± 0.20
20% 17FTMS/BTMOS/HCl	0.22 ± 0.07	<0.0001	2200 ± 700	–4.89 ± 0.17
20% AEMP3/MTMOS/Nafion (NO)[e,f]	0.10 ± 0.03	<0.0001	1000 ± 300	–5.79 ± 0.08

[a] The values were determined at 10 μM of NO and 100 μM of NO_2^- in deoxygenated PBS (0.01 M, pH 7.4), respectively. Data are represented as means ± SD (n = 3 or 5). [b] MTMOS, methyltrimethoxysilane; BTMOS, isobutyltrimethoxysilane; 3FTMS, (3,3,3-trifluoropropyl)trimethoxysilane; 9FTMS, nonafluorohexyltrimethoxysilane; 13FTMS, (tridecafluoro-1,1,2,2-tetrahydrooctyl)trimethoxysilane; 17FTMS, (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane; AEMP3, (aminoethylaminomethyl)phenethyltrimethoxysilane. [c] Xerogel compositions used: 45–75 μL of MTMOS or BTMOS, 0–30 μL of fluoroalkoxysilane (corresponding to 0–40%, balance MTMOS or BTMOS), 300 μL of ethanol, and 80 μL of water with or without 5 μL of 0.5 M HCl or 0.5 M NaOH as catalysts. All xerogel coatings were dried under ambient conditions for 24 h except the 17FTMS/BTMOS xerogel, which was cured at 80 °C for 24 h. [d] To determine NO selectivity over NO_2^-, the separate solution method was employed from Ref S7. [e] The previously-optimized composition of amine-modified xerogel coatings for a NO-permselective membrane from Ref S8. [f] The amine-modified xerogel membrane consists of 40 μL of MTMOS, 10 μL of AEMP3 (20%, balance MTMOS), 10 μL of Nafion (17% of 50 μL of total silane), 200 μL of ethanol, and 100 μL of water. After curing for 24 h under ambient conditions, the xerogel/Nafion-modified electrodes were then charged at 5 atm NO for 10 min.

Table S2. ^{29}Si chemical shifts (δ_{Si} in ppm from tetramethylsilane), relative intensities of T^n structures, and degrees of condensation (%*DC*) of 20% 17FTMS/MTMOS-derived xerogel membranes synthesized under different catalytic conditions[a,b]

	Si structure (int%)			
Catalytic condition	T^1 (–44 ppm)	T^2 (–53 ppm)	T^3 (–62 ppm)	%*DC*[c]
control[d]	5.2 ± 1.5	54.8 ± 0.5	40.0 ± 1.6	78.3 ± 1.7
6.5 mM HCl[e]	2.2 ± 0.6	36.3 ± 1.7	61.5 ± 1.8	86.4 ± 2.1
6.5 mM NaOH[e]	3.7 ± 0.8	22.1 ± 0.9	74.2 ± 2.3	90.2 ± 2.4

[a] The values were obtained by deconvolution of ^{29}Si CP/MAS NMR spectra. The peak intensity distributions were fitted to Gaussian functions, in terms of T^n where $n = 1$, 2, and 3 corresponding to the number of siloxane bridges bound to the silicon atom of interest. Data are represented as means ± SD ($n = 2$ or 3). [b] Xerogel composition used: 60 μL of MTMOS, 15 μL of 17FTMS (20%, balance MTMOS), 300 μL of ethanol, and 80 μL of water. All fluorinated xerogel coatings were dried under ambient conditions for 24 h. [c] The degree of condensation (%*DC*) was calculated from the relative intensities of T^n species. [d] Composition without a catalyst. [e] The addition of 5 μL of 0.5 M HCl or 0.5 M NaOH in the above xerogel composition, respectively.

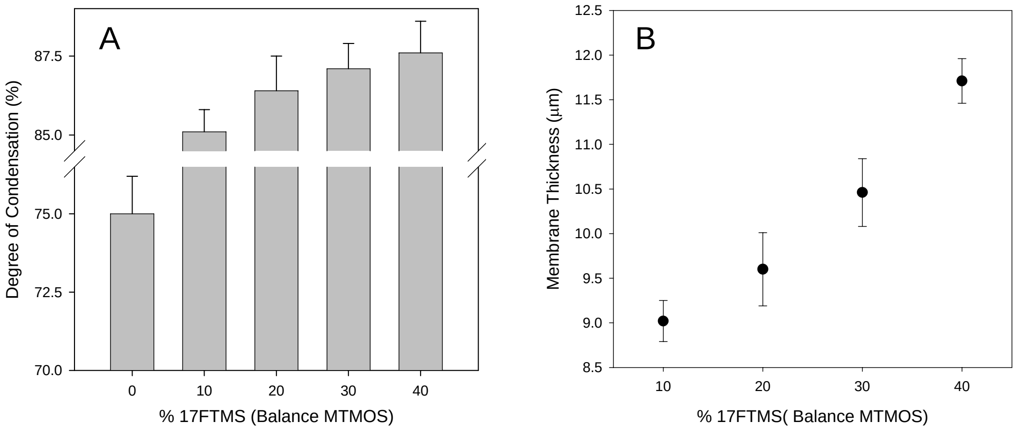

Figure S1. (A) Degree of condensation (%DC) and (B) thickness of the xerogel membrane as a function of the concentration of 17FTMS (balance MTMOS). All xerogels were synthesized under the acid-catalyzed conditions (6.5 mM HCl). The sol solution was deposited onto the Pt macroelectrodes (0.04 $\mu L \cdot mm^{-2}$) and allowed to cure for 24 h under ambient conditions. Data are represented as means ± SD ($n = 2$ or 3 for graph (A) and $n = 9$ for graph (B), respectively).

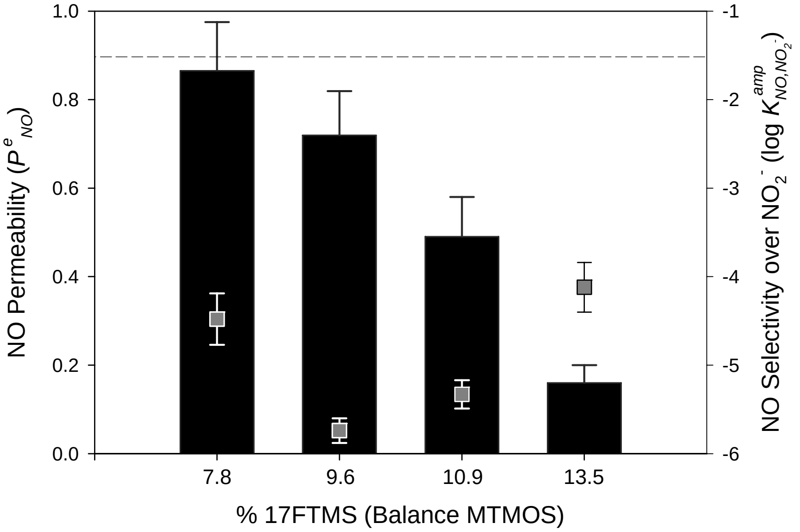

Figure S2. NO permeability (bar graphs, left axis) and selectivity over nitrite (scatter plots, right axis) as a function of the membrane thickness of 20% 17FTMS/MTMOS synthesized under the acid-catalyzed conditions (6.5 mM HCl). The dashed line indicates NO selectivity of the bare Pt electrode over nitrite. Data are represented as means ± SD (*n* = 3).

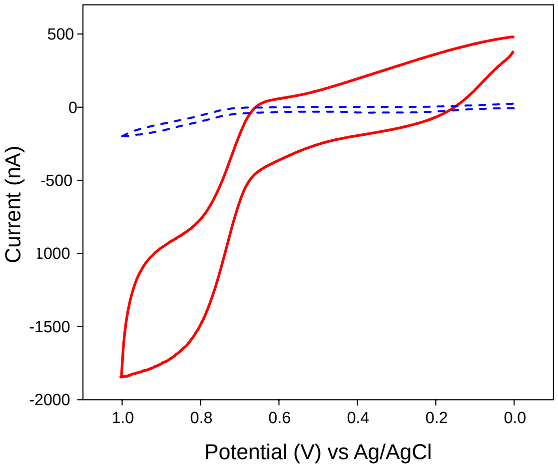

Figure S3. Cyclic voltammograms of the non-platinized (dashed blue) and platinized (solid red) Pt/W ultramicroelectrodes for 30 μM of NO in deoxygenated PBS (0.01 M, pH 7.4) at a scan rate of 100 mV·s^{-1} vs Ag/AgCl.

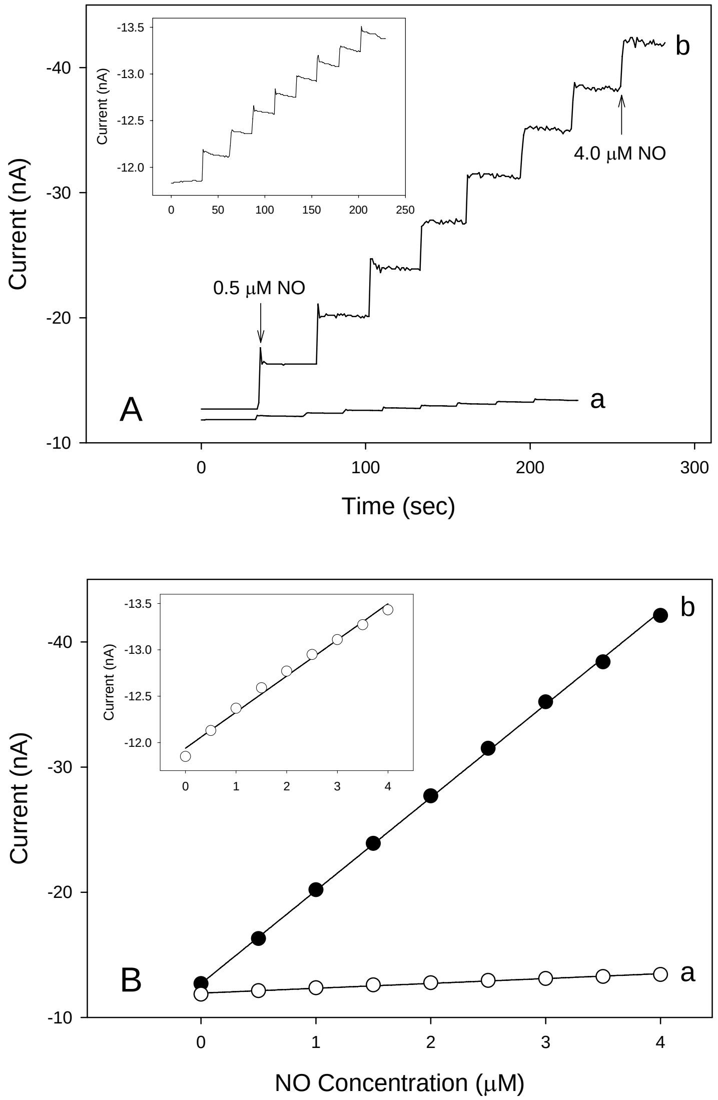

Figure S4. (A) Dynamic response and (B) calibration curves of the non-platinized (a) and platinized (b) Pt/W ultramicroelectrodes in deoxygenated PBS (0.01 M, pH 7.4). Currents were recorded at an applied potential of +0.7 and +0.8 V vs Ag/AgCl for the platinized and non-platinized electrodes, respectively. Insets represent the expansions of the dynamic response and calibration curves for the non-platinized electrode. The response sensitivity to NO was 0.38 (R^2 = 0.9948) and 7.38 (R^2 = 0.9998) nA·μM^{-1} for the non-platinized and platinized Pt/W ultramicroelectrodes, respectively.

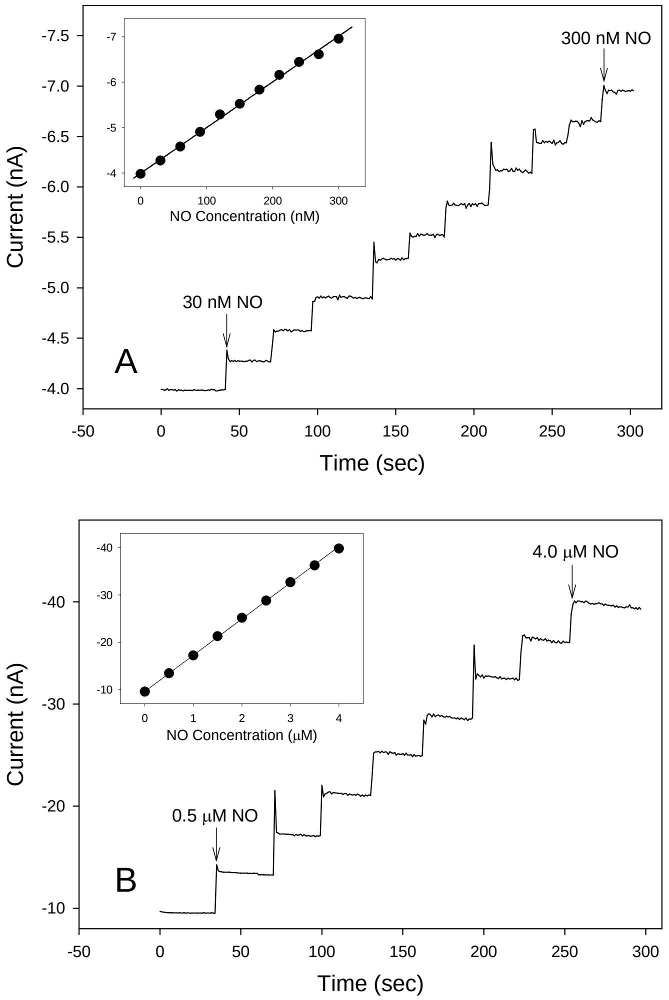

Figure S5. Dynamic response and calibration curves (insets) of the 20% 17FTMS/MTMOS-modified NO-selective ultramicroelectrode in the extended NO concentrations: (A) sub-micromolar and (B) micromolar levels of NO. The response sensitivity to NO was 9.96 pA·nM^{-1} ($R^2 = 0.9987$) in the range from 30 to 300 nM NO and 7.60 nA·μM^{-1} ($R^2 = 0.9999$) from 0.5 to 4.0 μM NO, respectively.

SI REFERENCES

S1. Lee, Y.; Oh, B. K.; Meyerhoff, M. E. *Anal. Chem.* **2004**, *76*, 536-544.
S2. Bedioui, F.; Trevin, S.; Devynck, J. *Electroanalysis* **1996**, *8*, 1085-1091.
S3. de Vooys, A. C. A.; Beltramo, G. L.; van Riet, B.; van Veen, J. A. R.; Koper, M. T. M. *Electrochim. Acta* **2004**, *49*, 1307-1314.
S4. Kitamura, Y.; Uzawa, T.; Oka, K.; Komai, Y.; Ogawa, H.; Takizawa, N.; Kobayashi, H.; Tanishita, K. *Anal. Chem.* **2000**, *72*, 2957-2962.
S5. Dean, J. A. *Lange's Handbook of Chemistry*, 15th ed.; McGraw-Hill: New York, 1999; pp 5.28.
S6. Dean, J. A. *Lange's Handbook of Chemistry*, 15th ed.; McGraw-Hill: New York, 1999; pp 5.6-5.7.
S7. Stefan, R.-I.; van Staden, J. F.; Aboul-Enein, H. Y. *Electrochemical Sensors in Bioanalysis*; Marcel Dekker: New York, 2001.
S8. Shin, J. H.; Weinman, S. W.; Schoenfisch, M. H. *Anal. Chem.* **2005**, *77*, 3494-3501.