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UNIVERSITY OF CALIFORNIA,
IRVINE

Lithographically Patterned Nanowires in Sensors and Transducers

DISSERTATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Chemical and Materials Physics

by

Rajen Kumar Dutta

Dissertation Committee:
Professor Reginald M. Penner, Chair
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2017

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DEDICATION

To my family, to my fiancée, and to all my friends: Thank you for your unending love and support.

TABLE OF CONTENTS

	Page
LIST OF FIGURES	iv
LIST OF TABLES	v
ACKNOWLEDGMENTS	vi
CURRICULUM VITAE	vii
ABSTRACT OF THE DISSERTATION	ix
1 Gold Nanowire Thermophones	1
1.1 Introduction	1
1.2 Experimental Methods	3
1.2.1 Chemicals and Materials	3
1.2.2 Fabrication of Gold Nanowire Thermophones	4
1.3 Acoustic Measurements	5
1.4 Results and Discussion	7
1.4.1 Sound Emission and Efficiency	7
1.4.2 Modeling Sound Emission	10
1.4.3 Effects of Input Power	14
1.5 Conclusion	16
2 Doped PEDOT Chemiresistor for Fast Sub-nanomolar Fe(III) Detection	17
2.1 Introduction	17
2.2 Chemicals and Materials	21
2.3 Nanojunction Fabrication	23
2.3.1 Embedded PEDOT-DFA Nanoreceptor	23
2.3.2 PEDOT-DFA Core-shell Nanojunction	28
2.4 Fe(III) Detection by Core-shell Nanojunction	31
2.4.1 Fe(III) Sensing Experiment	31
2.4.2 Results and Discussion	32
2.5 Conclusion	38
Bibliography	41

A	Appendix: Gold Nanowire Thermophones	46
A.1	Amplifier Design	46
A.2	Substrate Overheating	47
A.3	Constants Used in Calculation	48
B	Appendix: Doped PEDOT Chemiresistor	49
B.1	MATLAB Code	49
B.1.1	EIS	49
B.1.2	DC	51
B.2	Complete EIS Data for S1 and S2	53
B.2.1	S1	54
B.2.2	S2	59
B.2.3	Coefficient of Determination R^2 vs. Frequency	64

LIST OF FIGURES

	Page
1.1 Process Flow Diagram	4
1.2 Completed device and nanowire arrays	5
1.3 Nanowire width SEMs	6
1.4 Acoustic measurement setup	7
1.5 On-axis sound emission	8
1.6 Off-axis sound emission	9
1.7 Sound production efficiency	10
1.8 Analytical model fitting	13
1.9 Sound emission as a function of input power	15
2.1 Fe(III) Detection by PEDOT-DFA Nanowire Array	20
2.2 Nanoreceptor Process Flow	23
2.3 Nanogap Created by Focused Ion Beam	24
2.4 Completed Nanoreceptor Devices	25
2.5 Platinum Nanowire Electrodeposition	25
2.6 Pulsed PEDOT-DFA Electrodeposition	26
2.7 Nanojunction Process Flow	28
2.8 Completed Core-shell Nanojunction Devices	29
2.9 Nanowire cleaning in H_2SO_4	30
2.10 Electrodeposition of PEDOT-DFA Core-shell Nanojunction	31
2.11 SEMs of Nanogap and Core-shell Nanojunction	32
2.12 Nyquist Plots of Zn(II) and Fe(III) Response by S1	33
2.13 EIS Response at $f = 100$ Hz	34
2.14 DC Sensor Response to Zn(II) and Fe(III)	36
2.15 Equilibration of PEDOT-DFA Nanojunction in Background Electrolyte	37
2.16 Failure Modes of Core-shell Nanojunction	38
2.17 Third Generation Nanojunction Sensor	39

LIST OF TABLES

	Page
1.1 Literature Summary of Thermophone Devices and Performance Metrics . . .	3
1.2 Value of the fitting parameter, β_0 , in the calculations of Figure 1.9	14
2.1 Nanowire-based Chemiresistors and Transistors for the Detection of Metal Ions	22

ACKNOWLEDGMENTS

I would like to thank Brian Albee, Dr. Wytze E. van der Veer, Taylor Harville, Dr. Keith C. Donovan, Professor Dimitri Papamoschou, and Professor Reginald M. Penner for their support and assistance in my study of gold nanowire thermophones. I gratefully acknowledge the financial support of this work by the National Science Foundation Division of Chemistry through Contract CHE-1306928. Electron microscopy was performed at the LEXI facility at UCI and microphone measurements were collected at the Aeroacoustics Lab at UCI.

Chapter 1 adapted with permission from Dutta, Rajen, *et al.* “Gold Nanowire Thermophones.” *The Journal of Physical Chemistry C* 118.50 (2014): 29101-29107. Copyright 2014 American Chemical Society.

I would like to thank Victoria Lee, Dr. Mya Le, Crystin J. Eggers, and Professor Reginald M. Penner for their support and assistance in my study of doped PEDOT chemiresistors. I gratefully acknowledge the financial support of this work by Hitachi Chemical Co., Ltd. SEM, FIB, and EDS work was performed at the UC Irvine Materials Research Institute (IMRI) using instrumentation funded in part by the National Science Foundation Center for Chemistry at the Space-Time Limit (CHE-082913).

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Electrodeposited, Transverse Nanowire Electroluminescent Junctions

Shaopeng Qiao, Qiang Xu, **Rajen K. Dutta**, and Reginald M. Penner
ACS Nano 10 (2016) 8233

Distance-dependent Photo-induced Electron Transport in Nanometer-sized Junctions

Brian Albee, Xuejun Liu, Faezeh Tork Ladani, **Rajen K. Dutta**, and Eric O. Potma
Journal of Optics 18 (2016) 054004

100k Cycles and Beyond: Extraordinary Cycle Stability for MnO₂ Nanowires Imparted by a Gel Electrolyte

Mya Le Thai, Girija Chandran, **Rajen K. Dutta**, Xiaowei Li, and Reginald M. Penner
ACS Energy Letters 1 (2016) 57

A 30m Coaxial Nanowire Photoconductor Enabling Orthogonal Carrier Collection

Qiang Xu, Shaopeng Qiao, **Rajen Dutta**, Mya Le Thai, Xiaowei Li, Crystin J. Eggers, Girija Thesma Chandran, Zhengyun Wu, and Reginald M. Penner
Nano Letters 15 (2015) 5861

In Situ Electrical Conductivity of Li_xMnO₂ Nanowires as a Function of x and Size

Mya Le, Yu Liu, Hui Wang, **Rajen K. Dutta**, Wenbo Yan, John C. Hemminger, Ruqian Q. Wu, and Reginald M. Penner
Chemistry of Materials 27 (2015) 3494

Gold Nanowire Thermophones

Rajen Dutta, Brian Albee, Wytze E. van der Veer, Taylor Harville, Keith C. Donovan, Dimitri Papamoschou, and Reginald M. Penner
Journal of Physical Chemistry C 118 (2014) 29101

A Lithographically Patterned Capacitor with Horizontal Nanowires of Length 2.5 mm

Wenbo Yan, Mya Le Thai, **Rajen Dutta**, Xiaowei Li, Wendong Xing, and Reginald M. Penner
ACS Applied Materials & Interfaces 6 (2014) 5018

CONFERENCE PRESENTATIONS

Gold Nanowire Thermophones

MRS Spring Meeting & Exhibit

Apr 2015

ABSTRACT OF THE DISSERTATION

Lithographically Patterned Nanowires in Sensors and Transducers

By

Rajen Kumar Dutta

Doctor of Philosophy in Chemical and Materials Physics

University of California, Irvine, 2017

Professor Reginald M. Penner, Chair

Lithographically patterned metal nanowires were utilized in two studies on sensing and transduction. First, ultra-long (mm scale) polycrystalline gold nanowires were investigated for their ability to perform as thermophones, or thermoacoustic sound emitters. Arrays of ~ 4000 linear nanowires were fabricated at $5\text{ }\mu\text{m}$ pitch on glass surfaces. Sound generation by the nanowires was evaluated as a function of acoustic frequency (from 5 - 120 kHz), angle from the plane of the nanowires, input power (from 0.30 - 2.5 W) and the width of the nanowires in the array (from 270 to 500 nm.) Classical theory based upon metal films accurately predicts the measured properties of these gold nanowire arrays. Angular “nodes” for the off-axis sound pressure level (SPL) versus frequency data, predicted by the directivity factor, were faithfully reproduced by these nanowire arrays. The maximum efficiency of these arrays ($\sim 10^{-10}$ at 25 kHz), the power dependence, and the frequency dependence were independent of the lateral dimensions of these wires over the range from 270 to 500 nm. Second, a PEDOT-deferoxamine nanojunction chemiresistor was developed for the rapid detection of Fe(III) at sub-nanomolar concentrations. The backbone of the sensor is a single lithographically patterned metal nanowire in which a nanogap is formed by focused ion beam (FIB). The nanowire is then electrochemically reconnected by the ionophore-doped polymer PEDOT-deferoxamine, creating a chemically responsive junction selective for Fe(III). Fabrication challenges, centered on the adhesion between the metal

nanowire core and the PEDOT-DFA transduction layer, led to three design iterations of the sensor. Two of these nanojunctions were able to detect $10^{-11} - 10^{-4}$ M Fe(III), demonstrating a dynamic range that is on par with ion selective electrodes and a limit of detection that is three order of magnitude better. However, these junctions fail to decrease the detection time and show a significant response to the control ion Zn(II).

Chapter 1

Gold Nanowire Thermophones

1.1 Introduction

Adapted with permission from Dutta, Rajen, et al. "Gold Nanowire Thermophones." The Journal of Physical Chemistry C 118.50 (2014): 29101-29107. Copyright 2014 American Chemical Society.

Thermoacoustic speakers, also called thermophones, are transducers consisting of a low heat capacity conductor, such as a metal film. The application of an alternating current (ac) at a frequency ω to this conductor induces Joule heating of the conductor at a frequency 2ω . The resulting heat flux into the contacting air layer causes pressure oscillations that radiate as sound away from the conductor, also at a frequency of 2ω . Thus, thermophones are loudspeakers with no moving parts, and no magnets.

Arnold and Crandall¹ published a seminal paper on thermophones in 1917 that described many of the unique properties of these devices but in the nearly one hundred years since, interest in thermophones has waned. Then in 2008, Xiao *et al.*² demonstrated that freestand-

ing films of carbon nanotubes (CNTs) could function as thermophones and be transparent, flexible, and stretchable.² This work directed attention towards other types of nanomaterials capable of functioning as thermoacoustic transducers. Niskanen and Vesterinen *et al.*^{3,4} fabricated arrays of aluminum ribbons, $3\text{ }\mu\text{m}$ (w) $\times$ 30 nm (h), that were suspended across $200\text{ }\mu\text{m}$ trenches on a silicon surface. These devices produced frequency-dependent sound pressure levels in accord with theory and showed a maximum efficiency for sound generation of 3×10^{-6} at $\sim 40\text{ kHz}$.⁴ Tian *et al.*⁵ investigated the properties of films of thermally annealed silver nanowires randomly distributed on glass and polyethylene terephthalate (PET) surfaces. The individual silver nanowires in these films were $80\text{-}240\text{ nm}$ in diameter and $15\text{ }\mu\text{m}$, on average, in length. Efficiencies of up to 10^{-5} were obtained at $10\text{-}20\text{ kHz}$.⁵ Finally, Wei *et al.*⁶ fabricated thermophones from arrays of carbon nanotube “yarns” that were $\sim 30\text{ }\mu\text{m}$ in diameter and suspended across $600\text{ }\mu\text{m}$ grooves on a silicon substrate. The efficiency of this system was not reported, however.⁶ All other recent work of which we are aware (Table 1.1) has involved an evaluation of optically transparent films composed of metals,⁷ graphene,⁸ indium tin oxide (ITO)-coated glass,⁹ and the electronically conductive polymer PEDOT (poly(3,4-ethylenedioxythiophene)).¹⁰

The objective of our work was to characterize the properties of ultra-long (mm scale) polycrystalline gold nanowires as thermophones. Arrays of ~ 4000 linear, gold nanowires have been fabricated at $5\text{ }\mu\text{m}$ pitch on glass surfaces using lithographically patterned nanowire electrodeposition (LPNE).¹¹⁻¹³ As compared with films of silver nanowires investigated by Tian *et al.*⁵, these gold nanowire arrays have precisely defined lateral dimensions and nanowire-nanowire junctions are not present within the array. Such precisely defined gold nanowire arrays therefore afford an opportunity to quantitatively compare experimentally measured performance with the predictions of theory. The wire height in this study was maintained at a value of $100(\pm 8)\text{ nm}$ and a range of wire widths was explored, ranging from $270(\pm 14)$ to $500(\pm 28)\text{ nm}$. We found that classical theory for thermophones is remarkably accurate in predicting the behavior of gold nanowire arrays. Angular “nodes” for the off-

Table 1.1: Literature Summary of Thermophone Devices and Performance Metrics

Conductor ^a	Architecture	Substrate ^a	Efficiency	Ref
Al	suspended nanowire array	Si/air gap	3×10^{-6}	4
Pt	suspended film	—	nr	1
CNT	suspended film	—	nr	2
Al	film	porous Si	9×10^{-8}	7
CNT	suspended bundles	Si	nr	6
ITO	film	glass	6.3×10^{-8}	9
Graphene	film	paper	1×10^{-6}	8
PEDOT	film	glass	1.9×10^{-5}	10
Ag	nanowire mesh film	PET	2.1×10^{-5}	5
Au	nanowire array	glass	1.9×10^{-10}	This work

^aAbbreviations: CNT = carbon nanotube, ITO - indium tin oxide-coated glass, PEDOT = poly(3,4-ethylenedioxythiophene), PET = polyethylene terephthalate, nr = not reported

axis sound pressure level (SPL) versus frequency data, predicted by the directivity factor, are faithfully reproduced by these nanowire arrays. But the maximum efficiency of these arrays is low ($\sim 10^{-10}$ at 25 kHz) and independent of the wire width over the range of explored here.

1.2 Experimental Methods

1.2.1 Chemicals and Materials

Positive photoresist Shipley S-1808 and developer MF-319 were purchased from Microchem Corporation. Nickel wire (4 N purity, ESPI Metals), gold pellets (5 N purity, Kurt J. Lesker Co.) and chromium powder (3 N purity, American Elements) were used for the evaporation of films.

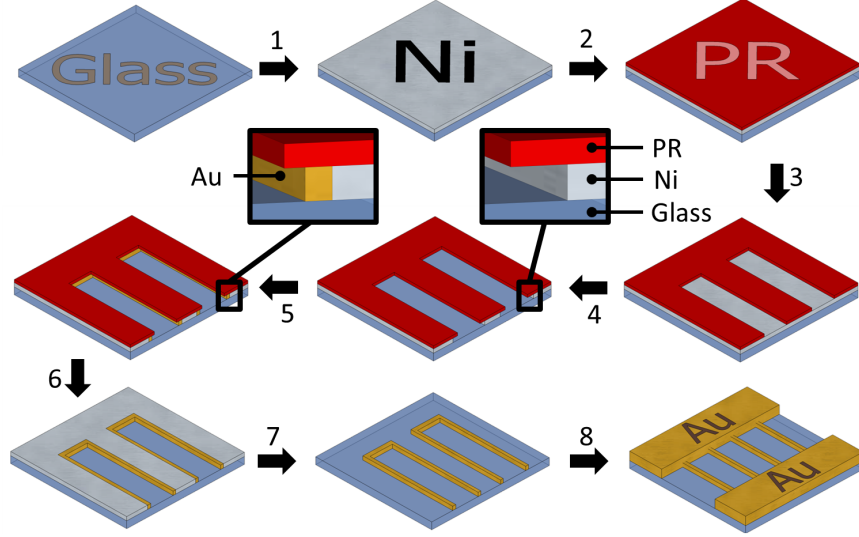


Figure 1.1: Process flow for the fabrication of thermophones consisting of an array of gold nanowires on glass using the Lithographically Patterned Nanowire Electrodeposition (LPNE) method.

1.2.2 Fabrication of Gold Nanowire Thermophones

Nanowire thermophone devices were fabricated using LPNE^{11–13}, as depicted in Figure 1.1. Starting with a clean soda lime glass slide, a 100 nm thick layer of nickel was thermally evaporated onto the surface (1). A layer of photoresist (PR) was then spin-coated onto the surface (2) and baked in a 90°C oven for 30 minutes. Using a contact mask with a 365 nm UV light source, shutter, and alignment stage (Newport, 83210i-line, 1.80s), the photoresist layer was patterned, then developed (3) for 30 s (Shipley, MF-319) and rinsed with Millipore water (Mill-Q, $\rho > 18 \text{ M}\Omega \cdot \text{cm}$). The exposed nickel was etched in 0.80 M nitric acid for 6 min to produce horizontal trenches below the photoresist edges (4). Gold nanowires were then electrodeposited into the trenches (5) by immersing the patterned chip into commercial Au plating solution (Clean Earth SolutionsTM). This electrodeposition was potentiostatic at -0.90 V vs. saturated calomel electrode (SCE) using a Gamry Series G 300 potentiostat in conjunction with a one compartment three-electrode electrochemical cell with Pt foil as counter electrode. Deposition times of 4, 6, 10, and 12 minutes were used to create arrays with different nanowire widths. After electrodeposition of the gold nanowires,

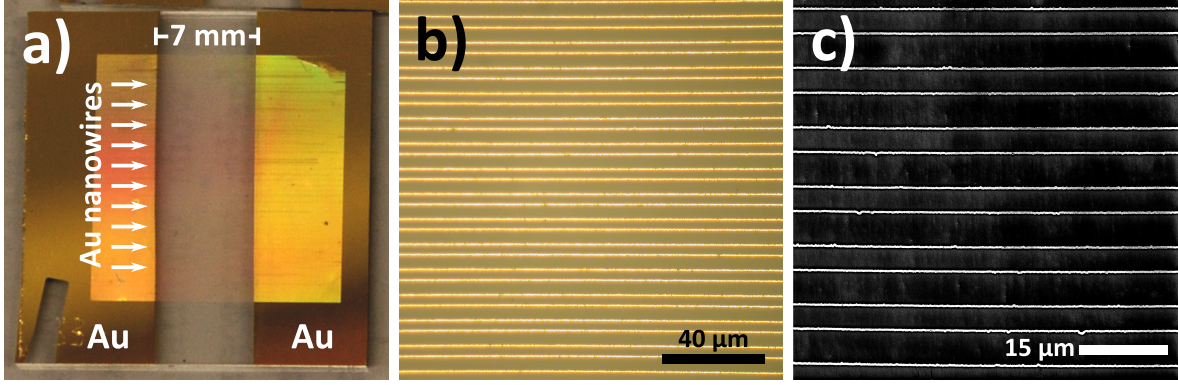


Figure 1.2: a) Optical image of the completed nanowire array on glass thermophone. b) Optical microscope image of the gold nanowire array. c) Scanning electron microscope image of the gold nanowire array.

the photoresist and nickel working electrode were removed by acetone rinse (6) and etching in 0.80 M nitric acid (7) respectively. Finally, the nanowire array is protected by a 7 mm wide strip of paper while 10 nm of chromium and 200 nm of gold are thermally evaporated to form the contacts (8). The completed device, seen in Figure 1.2a, is an array of up to 4000 parallel gold nanowires with a pitch of 5 μm . The resistance of the arrays ranged from 9.5 to 92 Ω . The devices were characterized using an FEI Magellan XHR SEM (extreme high-resolution scanning electron microscope) at an accelerating voltage of 1 kV. No metals were sputtered onto the devices for imaging. Figure 1.3 shows SEM images of these polycrystalline nanowires produced the by four different electrodeposition times.

1.3 Acoustic Measurements

The experimental setup is shown in Figure 1.4. The driving ac signal was a sinusoidal wave generated by an HP 33120A function generator, which was then fed into a homemade amplifier based on the Texas Instruments LM1875T chip (see Appendix A). Two Keithley 2000 digital multimeters were used to measure the ac current and voltage being supplied to the nanowire devices. With the exception of the amplifier, all of the above equipment

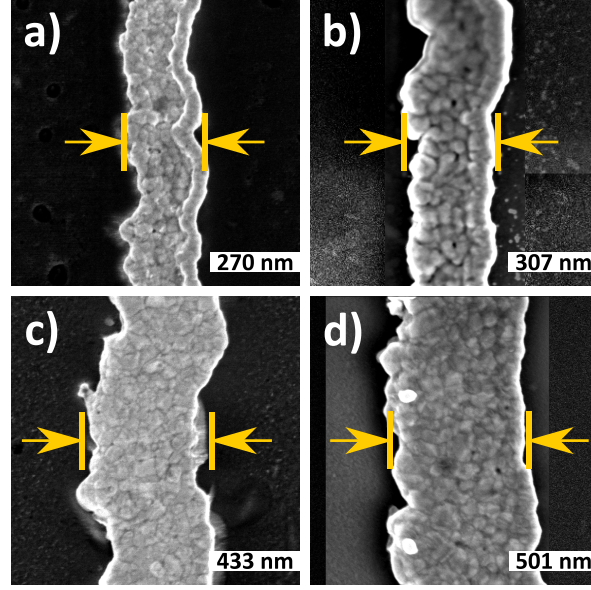


Figure 1.3: Scanning electron microscope images of gold nanowires showing the width range explored in this work. a) $270(\pm 14)$ nm, b) $307(\pm 21)$ nm, c) $433(\pm 57)$ nm, and d) $501(\pm 28)$ nm, where the values in parentheses are standard deviations. All nanowires were 100 nm in height.

was controlled through a LabVIEW program to supply the desired electrical power input to the thermophones. The acoustic output was measured by an array of seven 0.125 inch Brüel & Kjær Type 4138 condenser microphones, paired with Type 2670 preamplifiers. The microphones were held at various angles by a hemicylindrical anechoic dome with an outer diameter of 12 inches. The dome interior was lined with 2 inch wedge-shaped acoustic foam (Foam Factory, Inc.). The microphones were positioned with their tips 3 cm from the center of the nanowire thermophone. The thermophone sits on the stage in the xy -plane, with the nanowires running parallel to the x -axis. The microphones occupy the zx -plane. For each device, a background signal was first collected while no power was being supplied to the thermophone. This was later subtracted from the active signals. Correction factors for the microphones' actuator response (which accounts for the unique response profile of each microphone) and free-field response (which removes the interference of microphone with the sound field) were also applied. The measurements are also assumed to be in the acoustical far field. The boundary between the near and far field is typically approximated by the Rayleigh distance $R_0 = s/\lambda$, where s is the area of the sound source and λ is wavelength of

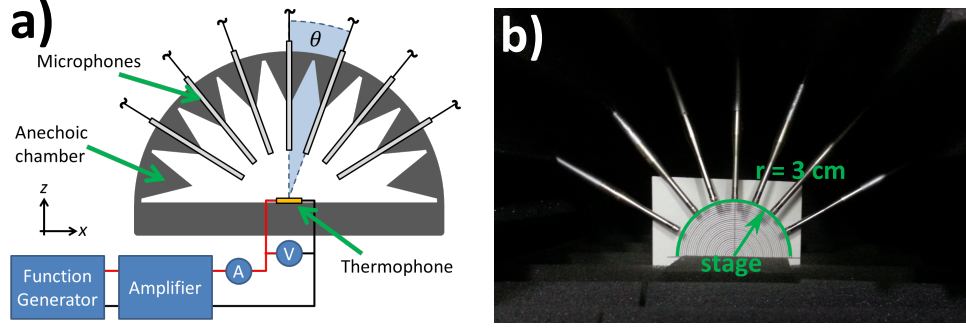


Figure 1.4: a) Diagram of the measurement setup. b) Optical image of the microphone array inside the anechoic dome with a calibration scale in place of the thermophone.

sound¹⁴. R_0 is typically interpreted as the distance from the sound source where the pressure waves take on spherical characteristics, but it has been argued that far field behavior occurs much earlier at $R_0/4$, which fully contains the measurement range of this experiment¹⁵.

1.4 Results and Discussion

1.4.1 Sound Emission and Efficiency

The sound pressure level as a function of output frequency generated by four nanowire arrays (from Figure 1.3) is shown in Figure 1.5. The SPL is defined as $20 \log_{10}(p/p_{ref})$, where p is the sound pressure and $p_{ref} = 20 \mu\text{Pa}$. Despite varying the width of the nanowires, and therefore the heat capacity, by nearly a factor of two, no discernible performance difference was observed for these nanowire arrays.

The geometry of the thermophone, a fixed surface (the substrate) with a “vibrating” subsection (the heated air layer), is similar to that of a piston in a fixed baffle plate. Sound radiated into half-space from a baffled piston exhibits characteristic interference patterns in the off-axis sound pressure when the dimensions of the piston are large compared to the wavelength of sound.¹⁴ These off-axis “nodes” are modeled by the directivity factor $D(\theta, \phi)$,

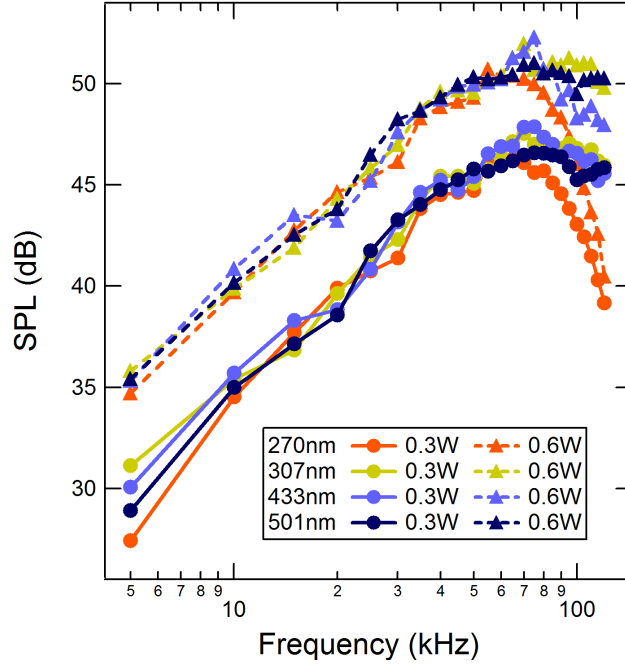


Figure 1.5: Sound pressure level vs. output frequency for nanowire arrays with input powers of 0.3 W (solid) and 0.6 W (dashed).

which is the ratio of the sound pressure at some angle θ, ϕ to the on-axis pressure at the same distance from the sound source. For the case of a rectangular piston, $D(\theta, \phi)$ takes the following form:⁴

$$D(\theta, \phi) = \text{sinc} \left(\frac{k_0 L_x}{2} \sin(\theta) \cos(\phi) \right) \text{sinc} \left(\frac{k_0 L_y}{2} \sin(\theta) \sin(\phi) \right) \quad (1.1)$$

where k_0 is the wavenumber $2\pi/\lambda$, and L_x and L_y are the dimensions of the piston surface. The microphones are defined to be in the $\phi = 0$ plane and their positions are described by θ , their angle with respect to the z -axis. Multiplying the on-axis pressure measurements, such as those in Figure 1.5, by the directivity factor produces an expected pressure amplitude at an angle θ . This is compared to the angular measurements of the 433 nm array in Figure 1.6.

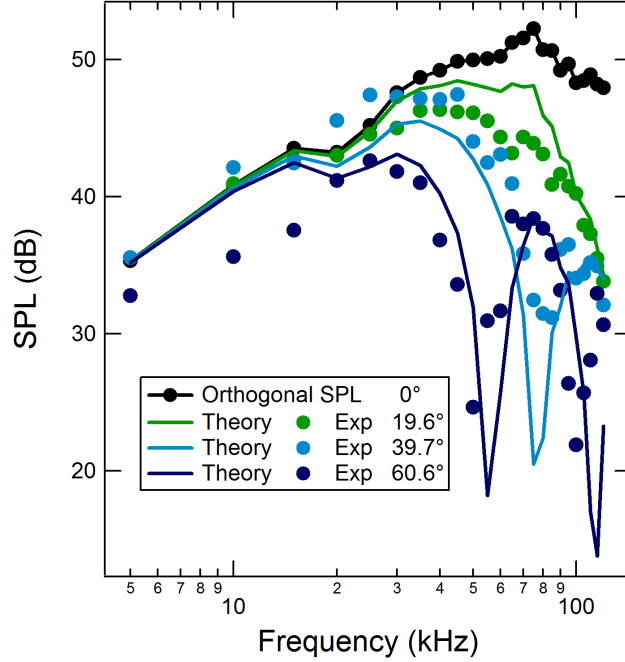


Figure 1.6: The off-axis SPL of a 100 nm (h) $\times$ 433 nm (w) nanowire array with $P_{in} = 0.6$ W. The measured SPL (dots) is compared to the expected level (lines) predicted by the directivity function $D(\theta, \phi)$ (Eq 1.1).

Since the directivity factor does appear to give an accurate description of the sound pressure in all space, it can be used to estimate the total acoustical power output. The acoustical power P_{ac} is given by:⁴

$$P_{ac} = \frac{p_{rms}^2(r, \theta = 0)r^2}{\rho_0 c_0} \int_0^{2\pi} \int_0^{\pi/2} D^2(\theta, \phi) \sin \theta d\theta d\phi \quad (1.2)$$

where $p_{rms}(r, \theta = 0)$ is the measured on-axis pressure at a distance of r from the device, and ρ_0 and c_0 are respectively the density and speed of sound in air at 25°C and 1 atm. Dividing this value by the electrical input power, we arrive at the efficiency values shown in Figure 1.7. The highest efficiency observed in this study, 1.9×10^{-10} , was achieved by a 515 nm array at 25 kHz with an input power of 2.5 W (Figure 1.9c). A general trend observed across the data of Figure 1.7a is that of increasing efficiency with increasing input power. This correlation is

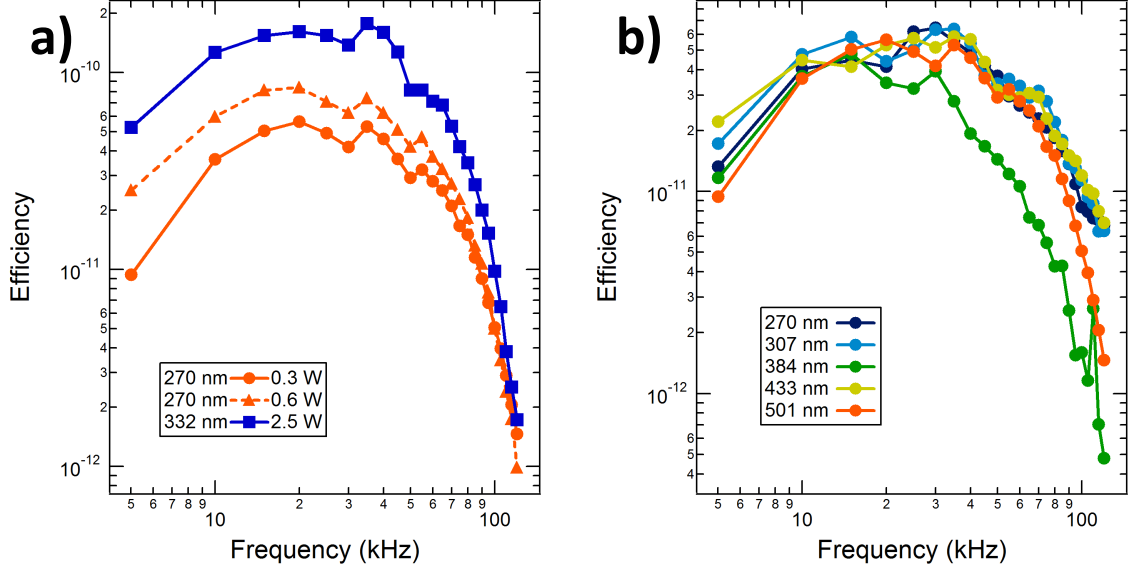


Figure 1.7: Plots of the efficiency as a function of frequency. a) Comparison of power-dependence for 0.3 W, 0.6 W, and 2.5 W. b) Comparison of four wire widths as indicated at $P_{in} = 0.3$ W. All nanowires were 100 nm in height.

expected since the system can be considered a heat engine following Carnot efficiency limit of $\eta \leq 1 - \frac{T_C}{T_H}$, where T_H is the temperature of the heat reservoir (nanowires) and T_C is the temperature of the cold reservoir (atmosphere). Since the different nanowire arrays produced remarkably similar SPL, it is not surprising that they also display very similar efficiencies across the measured frequency spectrum (Figure 1.7b).

1.4.2 Modeling Sound Emission

The original work of Arnold and Crandall¹ readily explains why an array of nanowires behaves like a metal film in terms of the thermoacoustic response. They surmised¹ that the cyclic heating of a boundary layer of air at the conductor surface generates pressure waves. They further hypothesized that the heated boundary layer could be modeled as a piston in place of the thermophone, and this hypothesis was supported by measurements of a thin Pt foil thermophone.¹ The radius of the heated boundary layer is defined to be one thermal wavelength, $\lambda_T = 2(\pi\alpha/f)^{1/2}$, from the conductor surface, where f is the frequency of thermal

wave and α is the thermal diffusivity of air. For nanowires, this region is approximated as a hemicylinder with a radius between 49 μm at 120 kHz and 238 μm at 5 kHz around each nanowire. Given that the nanowire array has a pitch of just 5 μm , the heated boundary layers from adjacent nanowires are overlapped. The result is that planar pressure waves are produced by the nanowire array in the acoustical near field, mimicking the behavior of metal film-based thermophones.

Improvements to this theory were later made by Xiao *et al.*² to more accurately describe the sound produced by an ultra-low heat capacity conductor like the CNT films in their study. Their expression for the root mean square pressure in the far field, p_{rms} , is:

$$p_{rms} = \frac{\alpha^{1/2} \rho_0}{2\pi^{1/2} T_0} \frac{P_{in}}{r} \frac{f^{1/2}}{C_s} \frac{f/f_2}{\left[(1 + (f/f_1)^{1/2})^2 + (f/f_2 + (f/f_1)^{1/2})^2 \right]^{1/2}} \quad (1.3)$$

where $f_1 = \alpha\beta_0^2/\pi\kappa^2$ and $f_2 = \beta_0/\pi C_s$. Here, α , ρ_0 , κ , and T_0 are the thermal diffusivity, density, thermal conductivity, and temperature of the ambient gas. P_{in} is the input power, and C_s is the heat capacity per unit area of the conductor. Finally, β_0 is the heat loss per unit area of the conductor per unit temperature above T_0 . In applying this analytical model to the data, β_0 was used as a fitting parameter. The plateau region in the SPL ($f > 70$ kHz), which is not predicted by the model, was excluded from the fitting calculation. Such plateaus at high frequencies are characteristic of thermophones and were first observed by Shinoda *et al.*⁷. This change in behavior usually attributed to near field interference¹⁶ or heterogeneous substrates, whether in the form of multiple layers⁷⁻⁹ or air domains⁶, but neither of these are present in our thermophone.

The resulting curve derived from Eq 1.3 (Figure 1.8, orange traces) fits our data poorly. Presumably, this is because the derivation of Eq 1.3 assumes the presence of air on both sides

of the surfaces of the conductor, whereas the nanowire arrays of interest here are supported on glass. This problem was solved by Vesterinen *et al.* who accounted for the effect of a substrate on the thermophone performance, redefining f_2 as:⁴

$$f_2 = \frac{\beta_0}{2\pi C_{s,sub}} = \frac{\beta_0}{2\pi C_{sub}} \left(\frac{f}{\pi \alpha_{sub}} \right)^{1/2} \quad (1.4)$$

where C_{sub} and α_{sub} are the heat capacity and thermal diffusivity of the substrate. Once again using β_0 as a fitting parameter, the resulting curve (Figure 1.8, blue traces) provides a much improved approximation of our data. The values of β_0 recovered from these fits are 2.1×10^5 W/(m²·K) and 2.5×10^5 W/(m²·K) for 0.3 W and 0.6 W, respectively. By comparison, a freestanding single-layer carbon nanotube film was reported to have a significantly lower β_0 of 28.9 W/(m²·K)², and β_0 has previously been shown to increase as a function of input power¹⁶ as seen here. Efficient diffusive transfer of heat by nanowires into the glass surface is expected based upon the hemicylindrical heat diffusion field in the glass that is dictated by the nanowire geometry.¹⁷ Anecdotaly, device “overheating” proved to be problematic for input powers of 2.5 W which sometime induced burning of the foam stage; for several devices, increasing the input power rapidly caused the glass substrate to shatter (see Appendix A for images). Since β_0 was determined as an adjustable parameter, it cannot be said with certainty how much these values represent the true losses in the system and how much they represent an incomplete description of the thermoacoustic effect. The choice of less thermally conductive substrates,^{5,8} and the suspension of the conductor in air,^{4,6} have been shown to improve thermophone performance (Table 1.1). Hu *et al.*¹⁸ also developed an analytical model for thermophone behavior that accounts for the substrate’s properties, although it ignores the properties of the conductor. Their expression for the root mean square pressure,

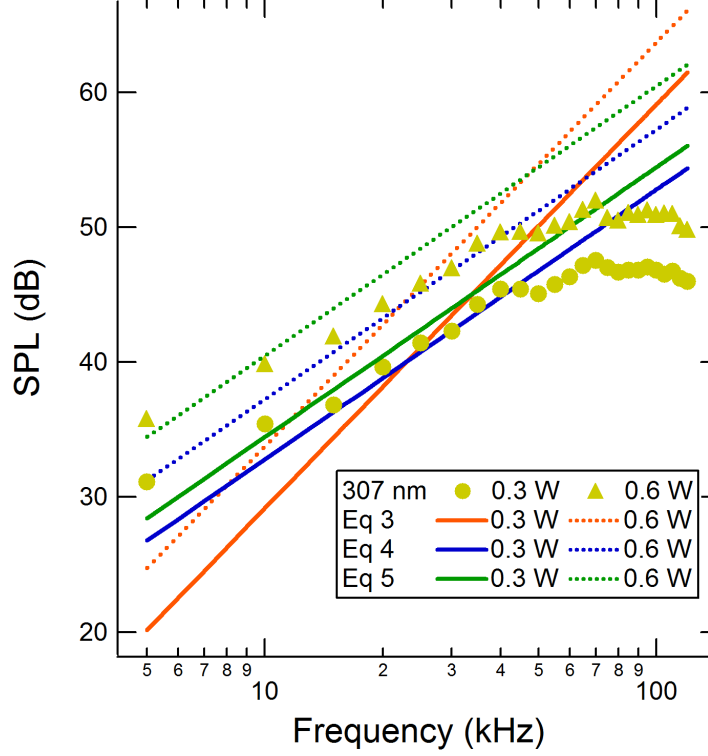


Figure 1.8: The analytical model described by Eq 1.3 (orange) and with the correction from Eq 4 (blue), both fitted to measurements from a 100 nm (h) $\times$ 307 nm (w) nanowire array. The model of Hu *et al.*¹⁸ (Eq 1.5) is shown in green.

translated into the far field, is

$$p_{rms} = \frac{R_0}{\sqrt{2}r} \frac{\gamma - 1}{v_g} \frac{e_g}{e_s + e_g} q_0 \quad (1.5)$$

where γ is the heat capacity ratio of air, v_g is the speed of sound in air, and e_g and e_s are the thermal effusivity of air and the substrate. The resulting curve is also shown in Figure 1.8. This model consistently overestimates the pressure amplitude generated by the thermophone, and the deviation seems to increase as a function of input power.

Table 1.2: Value of the fitting parameter, β_0 , in the calculations of Figure 1.9

f (kHz)	β_0 (10^5 W/m ² ·K) ^a
5	1.25
10	1.56
25	1.59
50	2.30
100	3.69

^a β_0 is the heat loss per unit area of the conductor per unit temperature above a reference temperature, T_0 .

1.4.3 Effects of Input Power

Figure 1.9 shows the performance of a 515 nm thermophone while increasing the input power from 0.5 W to 2.5 W. The curves shown are best fits using the correction above with the fit parameters shown in Table 1.2. For reference, the value of β_0 for SPL vs. frequency at 2.5 W for this device is 2.3×10^5 (MW/m²·K), similar to those seen as a function of power. Looking at sound pressure vs. power in Figure 1.9a, the expected linear relationship from Eq 1.3 holds by and large, although some deviation is seen at the highest powers and frequencies. This linear relationship has also been observed in several studies^{5,6,8–10} for $f \leq 50$ kHz and lower input powers of $P_{in} \leq 1.5$ W. The PEDOT thermophone¹⁰ was measured at similar input power densities (W/cm²) to those shown in this study, but the data was presented without a linear fit and cannot be conclusively compared to our data. Figure 1.9c shows the relationship between power, frequency, and efficiency for gold nanowire thermophones. As seen in Figure 1.7, the device efficiency increases with input power. Of these five frequencies measured, 25 kHz is produced most efficiently.

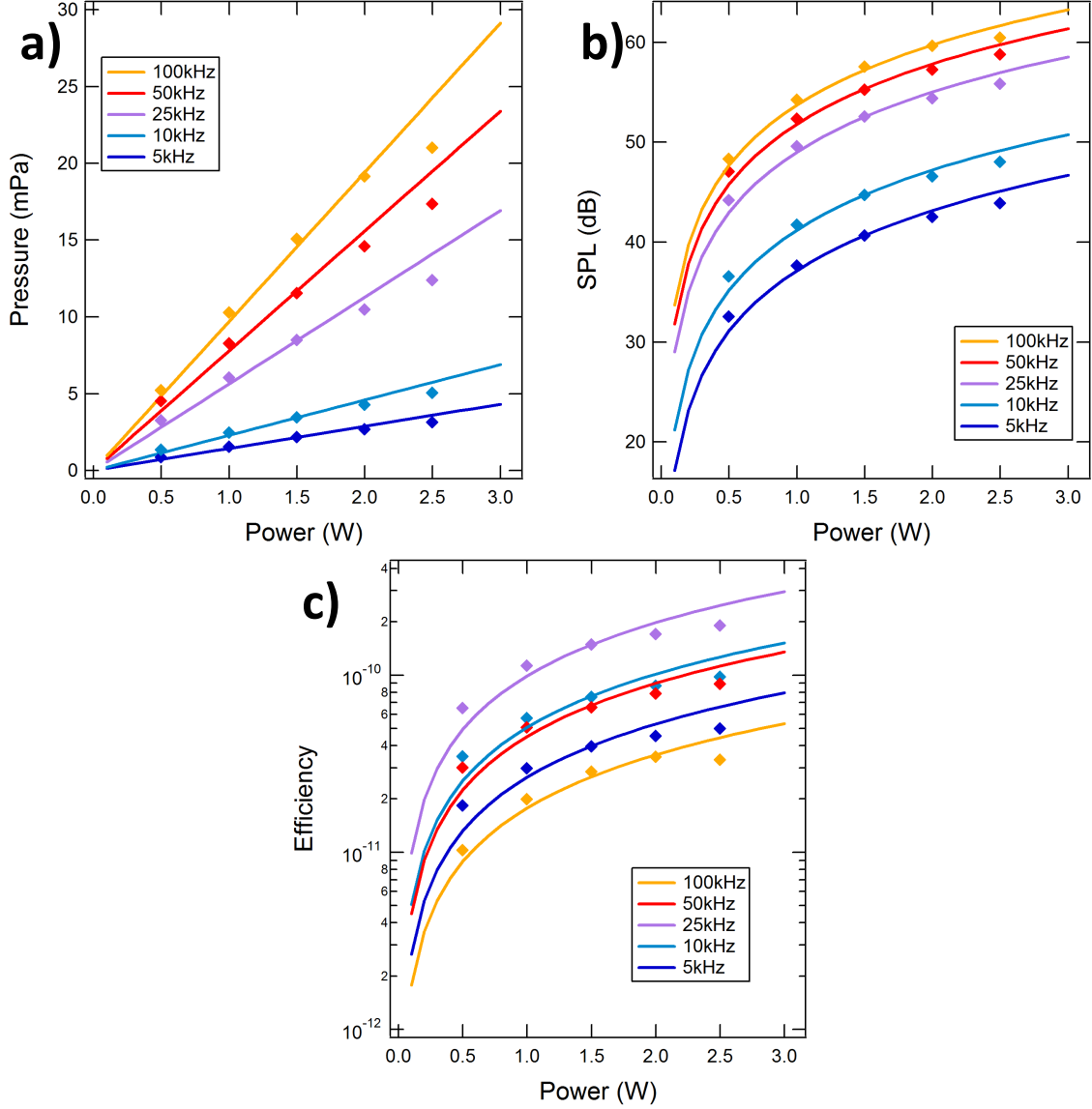


Figure 1.9: Comparison of theory for metal film thermophones with experimental data for a gold nanowire array (100 nm (h) $\times$ 512 nm (w)): a) Sound pressure, b) sound pressure level (SPL), and, c) efficiency as a function of input power. These data are presented at five frequencies as indicated. Solid curves are fits of Eq 4 to the experimental data. Parameters corresponding to the best fits are summarized in Table 1.2.

1.5 Conclusion

In this initial investigation of metal nanowire thermophones involving arrays of long (mm scale), noninteracting gold wires, the conclusion is that these nanowire arrays behave much like metal films in terms of their ability to produce sound using the thermoacoustic effect. In fact, in spite of the dramatically lower coverage of the glass surface by gold, θ_{Au} , which for the nanowire arrays investigated here is $0.054 < \theta_{Au} < 0.1$ depending upon the nanowire width, the properties of these nanowire arrays are accurately predicted by equations derived for metal film thermophones where $\theta_{Au} = 1.0$. Remarkably, even nuances such as angular “nodes” for the off-axis SPL versus frequency data, predicted by the directivity factor, are faithfully reproduced by these nanowire arrays. These nanowire arrays mimic the thermoacoustic behavior of metal films because the thermal wavelength, λ_T , at the surface of each nanowire is much larger than the distance between them, so the nanowire array generates a plane wave in the near field just like a film.

A lower efficiency for sound production is obtained from nanowires as compared with metal films (Table 1.1), likely reflecting the more efficient dissipation of the Joule heat in nanowires by hemicylindrical, rather than planar, diffusion from the nanowire into the glass surface.¹⁷ This picture is supported by the large values of β_0 , exceeding 10^5 W/(m²K), that we calculate for the nanowire arrays investigated in this study. Based upon this hypothesis, for metal nanowires systems where suspension of the nanowires away from the surface is possible, a dramatically elevated efficiency can be expected.

Chapter 2

Doped PEDOT Chemiresistor for Fast Sub-nanomolar Fe(III) Detection

2.1 Introduction

Iron is an earth abundant element¹⁹ that plays a key role in many aspects of biology and ecology. Almost all of the body's iron is found in hemoglobin, ferritin, and hemosiderin,²⁰ which are heavily involved in a number of body functions including oxygen transport and metabolism.²¹ Iron deficiency is the most common nutritional disorder in the world and is a significant issue in both industrialized and non-industrialized nations. This often leads to anemia, a low concentration of hemoglobin in the blood, which affects over 2 billion people globally.²² The possible effects of iron deficiency include stunted growth, lower resistance to infections, impaired mental function, decreased productivity, less efficient food-energy conversion, and impaired neural motor development.²³ Iron is found in the blood at a concentration of $10^{-7} - 10^{-6}$ M^{20,24} and has also been measured in sweat on the order of 10^{-7} M.²⁵ In the oceans, iron is found between 0.05 – 2 nM.²⁶ Limited availability of iron in ocean

waters has been linked to the limited growth and photosynthetic production by phytoplankton. These organisms are large-scale consumers of CO₂, therefore the concentration of iron in the oceans is believed to have a significant impact on global climate.²⁷

With small concentrations of iron playing such important roles in and out of the body, it is important to develop fast, sensitive, and portable analytical tools for quantitative study of the element. For many metal cations, an ion selective electrode (ISE) is capable of detecting the concentrations discussed above,^{28–30} but historically ISEs have only achieved a dependable limit of detection of 10^{-6} M for Fe(III).^{31–34} The technology is improving however: more recent work has been able to push the linear response range of ISEs down to 10^{-7} M Fe(III), with limits of detection (LoD) on the order of 10^{-8} M in the less dependable non-linear response region.^{35–38}

Ionophore-doped polymer nanowire chemiresistors offer a means to delivering a fast, sensitive, and selective sensor capable of meeting the diverse needs of iron sensing. Conducting polymers are of great interest for use in sensing because of their ability to transduce binding events into an electrical signal, tunable electrical conductivity, stability and biocompatibility, and relative ease of fabrication on the nanoscale through electropolymerization or electrospinning.^{39–41} Using small scale electrodes like nanowires offers further benefits in solution-based sensing. Small electrodes have reduced ohmic losses and allow for rapidly formed radial and cylindrical diffusion fields, leading to higher mass transport rates, current densities, and signal-to-noise ratios.⁴² Beginning in 1989 with Moutet,⁴³ polypyrrole was functionalized by amine groups to enhance its affinity to metal ions, most notably Ru(II). Shui *et al.*⁴⁴ then showed that covalently bonding these functional ligands to the polymer was unnecessary. Instead, the polymer could be doped with ionophores during electropolymerization, and they demonstrated that polypyrrole doped by bathophenanthroline disulfonate and bathocuproine disulfonate was sensitive to Cu(I) and Cu(II), with a LoD of 2 μ M detectable by square-wave voltammetry of the polymer electrode. Lin *et al.* were among those to being

using polymer nanostructures, making nanowire⁴⁵ and nanotube⁴⁶ electrodes of tripeptide-modified polypyrrole to selectively detect Cu(II) by square wave voltammetry, achieving LoDs of 20 nM and 100 nM, respectively. The problem of metal ion sensing naturally lends itself towards field effect transistor (FET)-based devices: these recent works are summarized in Table 2.1. Surprisingly, there are very few nanoscale polymer chemiresistors that have been developed for metal ion sensing. Zhang *et al.* sandwiched a thin film of oligopeptide-doped polyaniline in a metal nanogap, allowing them to use conductivity measurements to detect Cu²⁺ down to 100 pM.⁴⁷ The only other chemiresistor comes from Aravinda et al., who used a single polypyrrole nanotube doped by nitrilotriacetic acid (NTA) to detect as little as 10⁻¹⁴ M Cu²⁺.⁴⁸

The primary inspiration for this study comes from previous work within our group by Kindra *et al.*⁴⁹ An array of lithographically patterned electrodeposited nanowires was fabricated out of poly(3,4-ethylenedioxythiophene) (PEDOT) in the presence of iron chelator deferoxamine (DFA), doping the nanowires with the Fe(III)-selective ionophore. The array was then exposed to a series of concentrations of Fe(III) and Zn(II), the results of which are shown in Figure 2.1. The nanowire array showed strong sensitivity and selectivity for Fe(III), with a measured LoD of 10 nM, and a theoretical LoD of 300 pM. Very little change in resistance was observed for the chemiresistor in the presence of Zn(II), and there was a near nonexistent response by a PEDOT nanowire array that was not doped by DFA. While this sensor is extremely competitive, beating the LoD of ISEs, it required 20 minutes of equilibration while a typical ISE response time is under 30 s. A key hindrance to the sensor performance is the large resistance of the PEDOT-DFA nanowire. Combined with the fact that the large nanowire array also likely creates a planar diffusion field, the conditions for fast mass transport both in the solution and in the nanowires are not optimal. The array is also vulnerable to variability between the individual nanowires: just one nanowire with poor sensitivity can dampen the response of the entire array due their parallel configuration. Reducing the array to a single element and shrinking the high resistive transducer can

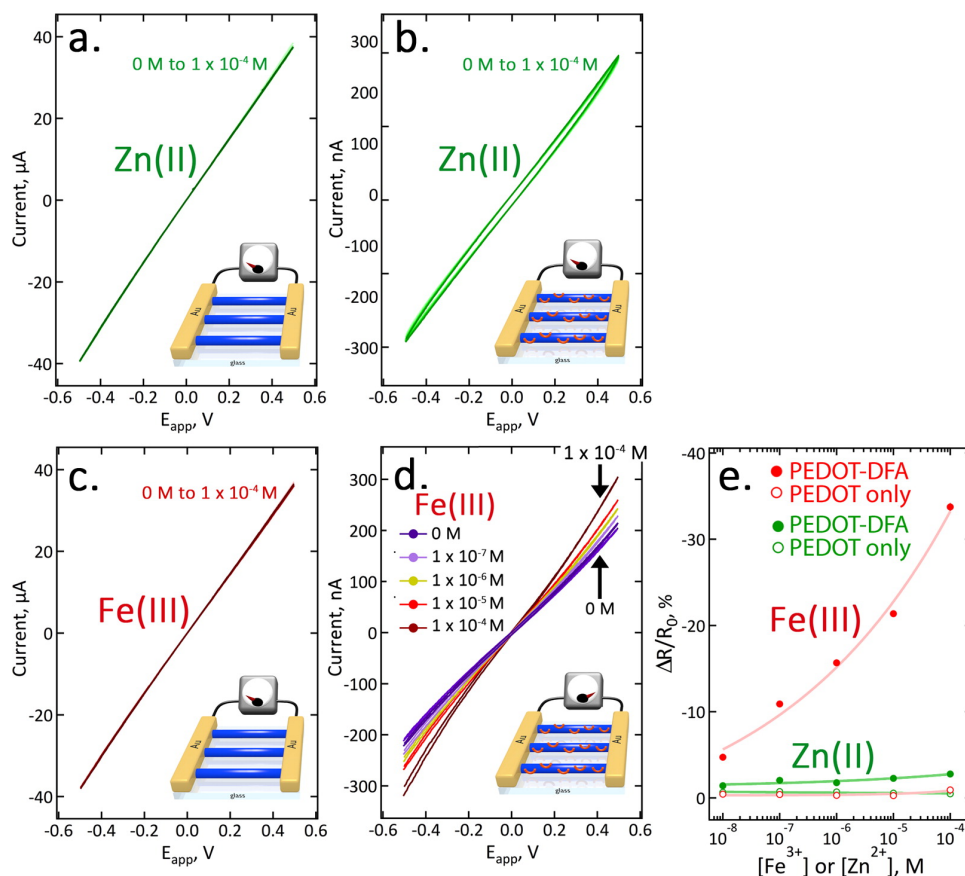


Figure 2.1: Current versus voltage (IV) curves for PEDOT (a, c) and PEDOT-DFA (b, d) nanowire arrays. (a, b) IV curves acquired in five Zn(II) solutions ($[\text{Zn(II)}] = 10^7, 10^6, 10^5$, and 10^4 M) at pure PEDOT nanowires (a) and PEDOTDFA nanowires (b). All scan rates were 20 mV/s. (c, d) IV curves acquired in five Fe(III) solutions ($[\text{Fe(III)}] = 0, 10^7, 10^6, 10^5$, and 10^4 M) at pure PEDOT nanowires (c) and PEDOTDFA nanowires (d). All scan rates were 20 mV/s. (e) Plot of the change in the measured resistance, R , normalized by the initial resistance, R_0 , as a function of $[\text{Zn(II)}]$ and $[\text{Fe(III)}]$. Controls (open red circles) are the responses seen for pure PEDOT-only nanowires and (open green circles) and the electrical contacts without any nanowires. Reprinted with permission © 2015 American Chemical Society⁴⁹

improve mass transport throughout the system and reduce ohmic losses, which would improve both the response time and the signal-to-noise ratio.

This chapter presents a PEDOT-DFA nanojunction chemiresistor for the rapid detection of Fe(III) at sub-nanomolar concentrations derived from the above design considerations. The backbone of the sensor is a single lithographically patterned metal nanowire in which a nanogap is formed. The nanowire is then electrochemically reconnected by the ionophore-doped polymer, creating a chemically responsive junction selective for Fe(III). Two of these nanojunctions were able to detect $10^{-11} - 10^{-4}$ M Fe(III), demonstrating a dynamic range on par with ISEs as well as a better limit of detection. However, these junctions fail to improve the detection response time and show a significant response to the control ion Zn(II).

2.2 Chemicals and Materials

Positive photoresist S-1808 (Microchem), developer MF-319 (Microchem), Thinner P (Rohm Haas), and acetone (ACS grade, Fisher Scientific) were used for photolithography. Gold and nickel pellets (99.999%, Kurt J. Lesker Co.) and chromium powder (99.9%, American Elements) were used as evaporation sources for thin films. Nickel was etched using HNO_3 (ACS grade, Macron). I_2 (Allied Chemical) and KI (ACS grade, Sigma Aldrich) were used in the gold etchant. Glass was cleaned in Nochromix (Godex Labs) and H_2SO_4 (ACS Grade, Macron). K_2PtCl_6 (98%, Sigma Aldrich) and KCl (ACS grade, Sigma Aldrich) were used in platinum electrodeposition. EDOT (97%, Sigma Aldrich), LiClO_4 (99%, Acros Organics), and deferoxamine (92.5%, Sigma Aldrich) were used in the electrodeposition of PEDOT-DFA. Nanowire cycling was done using H_2SO_4 (99.999%, Sigma Aldrich). NaNO_3 (99.999%, Sigma Aldrich), HNO_3 (99.999%, Sigma Aldrich), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.99%, Sigma Aldrich), and $\text{Zn}(\text{NO}_3)_2$ hydrate (99.999%, Sigma Aldrich) were used in the analyte solutions. All aqueous solutions and rinsing used Millipore water (Mill-Q, $\rho > 18 \text{ M}\Omega \cdot \text{cm}$).

Table 2.1: Nanowire-based Chemiresistors and Transistors for the Detection of Metal Ions^{a,b}

nanowire description	ionophore	detected metal ions	conc. range	LoD _{Mⁿ⁺}	ref
<i>semiconductor</i>					
silicon FET	calmodulin	Ca ²⁺	25 μ M only	$\approx 5\mu$ M (est.)	50
silicon FET	tripeptide	Cu ²⁺	10 ⁻⁹ to 10 ⁻² M	1 nM (est.)	51
silicon FET	oligopeptide	Cu ²⁺ , Pb ²⁺	n.a.	1 nM (Cu ²⁺) 10 nM (Pb ²⁺)	52
silicon FET	3-(mercaptopropyl) triethoxysilane	Cd ²⁺ , Hg ²⁺	10 ⁻⁴ to 10 ⁻² M (Hg ²⁺) 10 ⁻⁷ to 10 ⁻³ M (Cd ²⁺)	10 mM (Hg ²⁺) 0.10 μ M (Cd ²⁺)	53
carbon SWNT FET	PANI/oligopeptide	Cu ²⁺	10 ⁻¹⁰ to 10 ⁻⁶ M	1 pM	54
	PPy/oligopeptide	Ni ²⁺	10 ⁻¹⁰ to 10 ⁻⁶ M	60 pM	
rGO FET	calmodulin	Ca ²⁺ , Hg ²⁺	10 ⁻⁶ to 10 ⁻⁴ M (Ca ²⁺) 10 ⁻⁹ to 10 ⁻⁷ M (Hg ²⁺)	1 μ M (Ca ²⁺) 1 nM (Hg ²⁺)	55
<i>polymer</i>					
PPy NWs	tripeptide	Cu ²⁺	10 ⁻⁸ to 10 ⁻⁶ M	20 nM	45
PPy NTs	tripeptide	Cu ²⁺	10 ⁻⁷ to 10 ⁻⁵ M	100 nM	46
PANI CR	oligopeptide	Cu ²⁺	10 ⁻¹⁰ to 10 ⁻⁹ M	100 pM	47
PPy SNT CR	NTA	Cu ²⁺	10 ⁻¹⁴ to 10 ⁻¹⁰ M	60 fM	48
PEDOT NWs CR	DFA	Fe ³⁺	10 ⁻⁸ to 10 ⁻⁴ M	10 nM	49
PEDOT NJ CR	DFA	Fe ³⁺	10 ⁻¹¹ to 10 ⁻⁴ M	10 pM	this work

^aAbbreviations: FET, field-effect transistor; CR, chemiresistor; NWs, nanowires; NTs, nanotubes; SNT, single nanotube; NJ, nanojunction; PPy, polypyrrole; PANI, polyaniline; rGO, reduced graphene oxide; PEDOT, poly(3,4-ethylenedioxythiophene); NTA, nitrilotriacetic acid; DFA, deferoxamine; LoD_{Mⁿ⁺}, limit of detection.^bMeasured response was attributed to both anion and cation.

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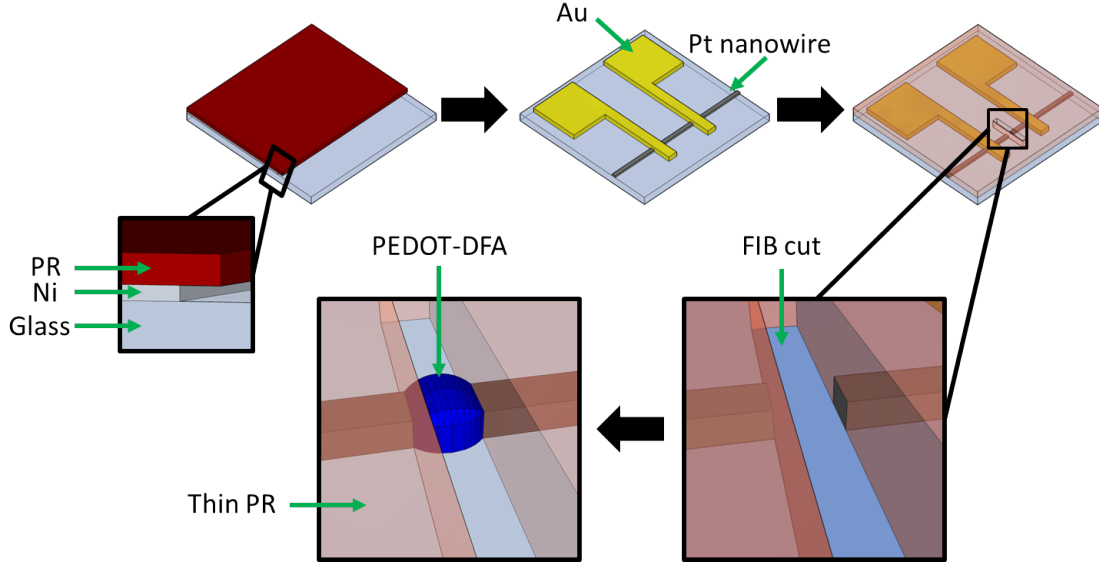


Figure 2.2: Process flow for fabrication of the embedded PEDOT-DFA nanoreceptor.

2.3 Nanojunction Fabrication

2.3.1 Embedded PEDOT-DFA Nanoreceptor

The fabrication of the PEDOT-DFA nanoreceptor chemiresistor begins with Lithographically Patterned Nanowire Electrodeposition (LPNE)^{11–13} in order to make the single platinum nanowire that is the backbone of the device. The process begins with an inch by inch glass slide cleaned in Nochromix solution. A 40 nm thin film of nickel metal was physically vapor deposited (PVD), after which a layer of photoresist (S-1808) was spin-coated on and the slide baked in a 90°C oven for 30 minutes. The photoresist layer was then patterned using a contact mask with a 365 nm UV light source, shutter, and alignment stage (Newport, 83210 i-line, 2.20 s), and developed for 30 s (MF-319). The nickel film was then etched in 0.8 M HNO₃ for five minutes, removing all exposed metal and producing the undercut trench seen in the start of Figure 2.2. Platinum was then electrodeposited into the trench, after which the photoresist layer and nickel film were removed by acetone and 0.8 M HNO₃, respectively. Photoresist residues were removed by an oxygen plasma (Harrick Plasma PDC-32G, 11 W, 5

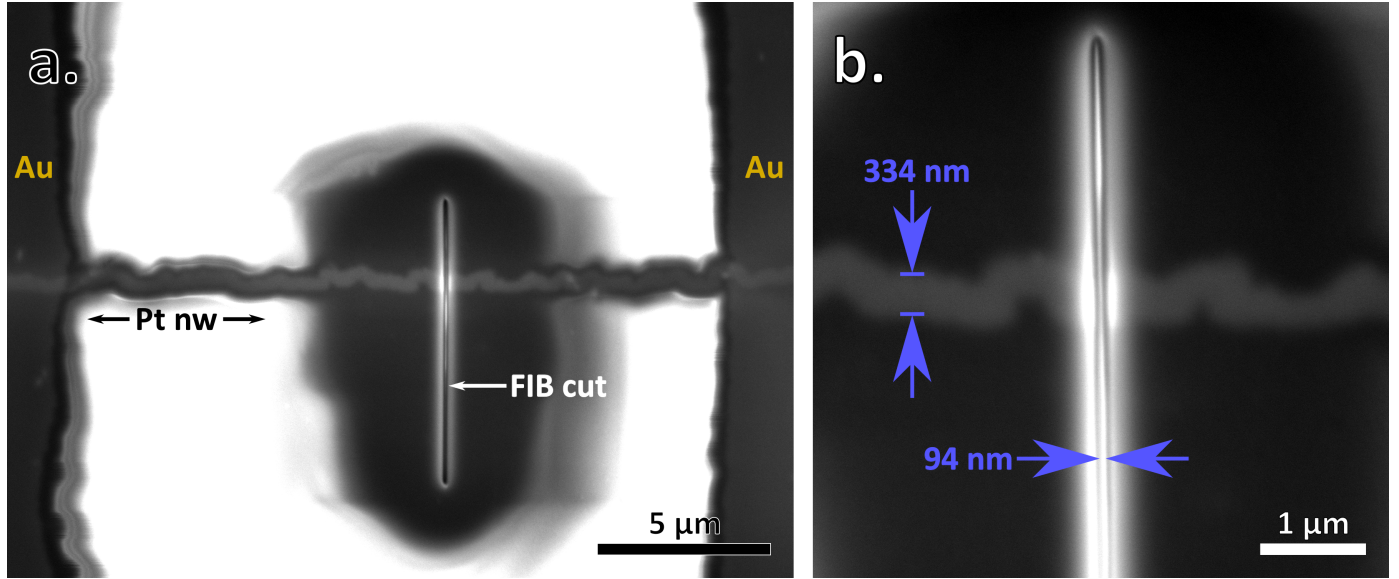


Figure 2.3: (a) Secondary electron image of the Pt nanowire and the Au contacts, entirely covered by thinned photoresist except for the FIB cut at the center. (b) Magnified electron microscope image of the FIB cut region. The cut measures 94 nm across.

min), after which the slide was covered in a 100 nm gold film by PVD. The electrical contacts were formed by spin-coating, baking, patterning, and developing another S-1808 photoresist layer, then etching in the exposed gold film in tri-iodide etchant (30 s in 4 g KI, 2 g I₂, 80 g H₂O) and rinsing with acetone. The slide was then insulated in a final photoresist layer, which was diluted by 2 parts of solvent (Thinner P). The thinned photoresist layer enabled greater ease of viewing the covered nanowire with an electron microscope. A 30 kV, 10 pA focused ion beam (FIB) was used to slice through the photoresist and cut a 100 nm gap in the nanowire (FEI Quanta 3D FEG Dual Beam Microscope), as seen in Figure 2.3. Even with the thinned photoresist layer, it was extremely difficult to image the nanowire under the ion beam, so a long (6 μm) pattern was used to ensure the nanowire was not missed. Finally, the chemiresistor device was completed by reconnecting the nanowire by electrodepositing PEDOT-DFA transducing element in the nanogap. The completed slide, seen in Figure 2.4, has a capacity of six nanowire sensors.

The platinum metal electrodeposition was done in a three-electrode electrochemical cell, using the nickel thin film as the working electrode, a platinum flag counter electrode, and

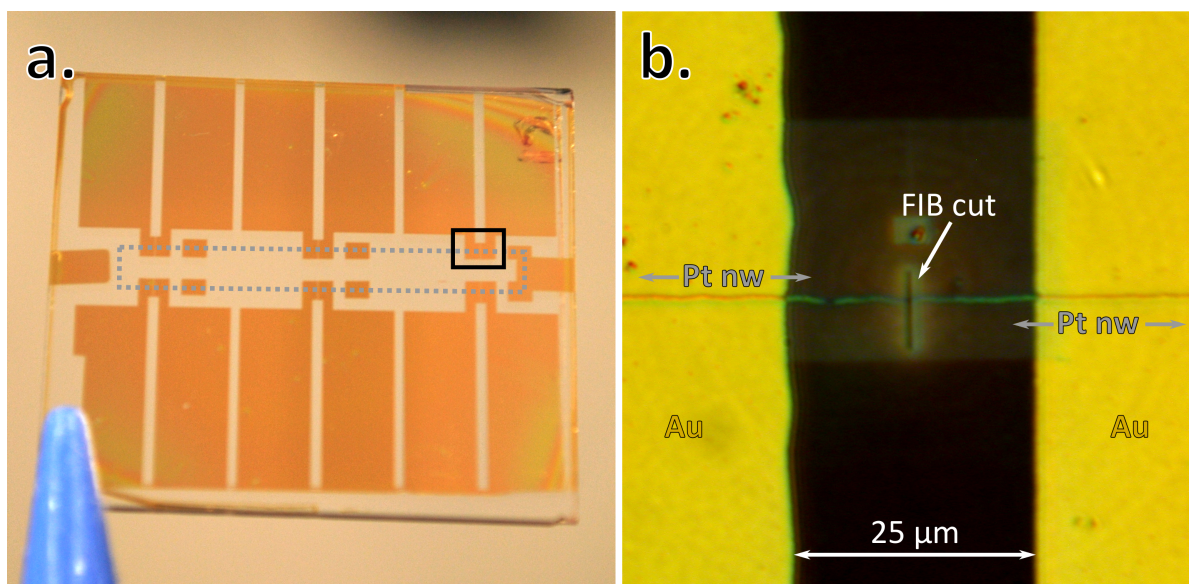


Figure 2.4: (a) Image of the completed slide containing six embedded nanoreceptor devices with a black box around one such device. The dotted gray line indicates the platinum nanowire. (b) Optical microscope image of a single embedded nanoreceptor chemiresistor device. Each nanowire spans the $20\ \mu\text{m}$ gap between the contact pads

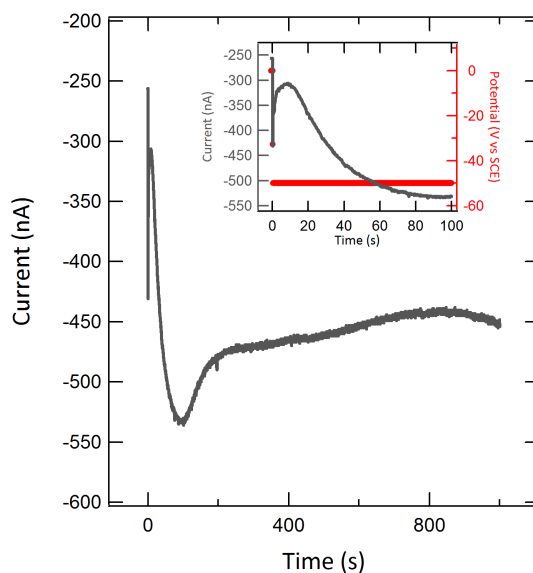


Figure 2.5: Potentiostatic electrodeposition of platinum metal in the LPNE template. Inset: magnified current and voltage traces during the initial nucleation of the Ni thin film edge.

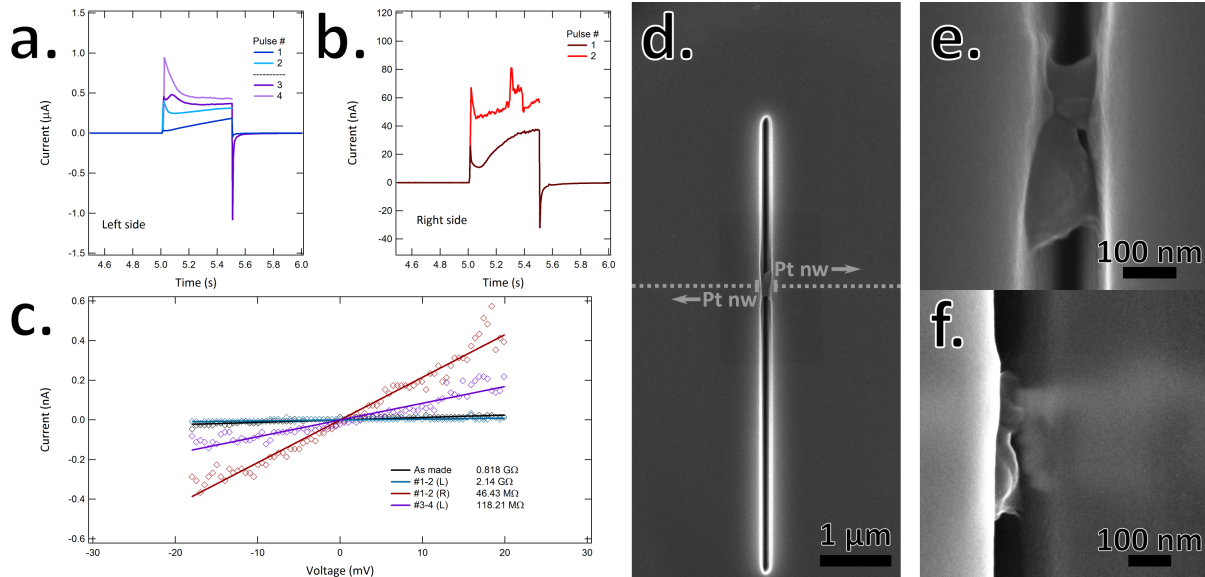


Figure 2.6: Current vs. time traces of the voltage pulses applied to the (a) left and (b) right ends of the Pt nanowire in the nanogap. (c) IV characterization between each set of voltage pulses. (d) SEM image of the FIB cut region after PEDOT-DFA deposition. The dashed gray line denotes the Pt nanowire below the surface (not visible with only 1 kV accelerating voltage). (e) Close-up SEM image of the embedded PEDOT-DFA nanoreceptor. (f) Another SEM image of the nanoreceptor tilted 30° from orthogonal under a 10 kV beam, making the right Pt nanowire visible through the photoresist layer.

a saturated calomel electrode (SCE) reference. A potential of -0.50 V vs. SCE was applied to the nickel film in a solution of 1 mM K_2PtCl_6 and 0.1 M KCl. Figure 2.5 shows the current vs. time trace resulting from the reduction of platinum in the LPNE trench. Two characteristics of LPNE can be seen in this data. First is the rapidly increasing reduction current in approximately the first 100 s of voltage application, corresponding to platinum nucleating and populating the nickel film edge. Second is the quasi-constant current seen after 200 s of deposition, caused by a combination of a kinetically controlled reaction and a constant surface area presented to the solution by the platinum nanowire as it fills the trench.¹¹

The electrodeposition of the PEDOT-DFA nanoreceptor was done in the same three-electrode configuration as the platinum nanowire, with the exposed tips of the nanowire acting as the working electrode. While PEDOT is usually deposited through cyclic voltam-

metry, even a single cycle would deposit far too much material on the incredibly small surface area presented by the exposed nanowire ends. Pulsed chronoamperometry was used instead to give the needed temporal resolution. In a solution of 12.5 mM LiClO_4 , 5 mM EDOT, and 1 mM DFA, the electrode was held at open circuit voltage (OCV) for 5 s, followed by the pulse step of 1.1 V vs. SCE for 0.5 s. Figures 2.6a and b show the oxidation current during the voltage pulse. The polymer was deposited in sets of two pulses alternating between the left and right sides of the nanogap. In between each set of pulses, the IV response across the nanogap was measured in the plating solution (Figure 2.6c). The conductivity across the gap jumped up sharply after two deposition pulses to each side of the gap, though it oddly decreases after an additional set. On other devices (data not shown), further deposition did not improve the conductivity of the junction, therefore the junction is considered electrically reconnected by PEDOT-DFA at this point. The quality of the reconnection appears to be poor, however. Given PEDOT-DFA is estimated to have a resistivity of $68 \text{ } \Omega\text{cm}$,⁴⁹ an embedded PEDOT-DFA nanoreceptor ($100 \text{ nm } l \times 300 \text{ nm } w \times 40 \text{ nm } h$) would have a resistance of only $5.7 \text{ M}\Omega$. The platinum nanowire only contributes a negligible $5 \text{ k}\Omega$ in addition. SEMs of the nanoreceptor (Figure 2.6d-f) show that the PEDOT-DFA polymerized on the nanowire ends and spanned the FIB gap. The stage was tilted and the accelerating voltage increased to 10 kV in order to view the nanowire in Figure 2.6f. The Pt edge appears to have little to no direct contact with the PEDOT-DFA, which is likely the source for the very low deposition current shown in Figure 2.6b and a contributor to the higher than expected resistance of the nanojunction. The FIB cut creates an amorphous edge out of the photoresist, obscuring the Pt nanowire electrode and often leading to nanojunction resistances on the order of hundreds of $\text{M}\Omega$ to $\text{G}\Omega$. This necessitated a redesign of the chemiresistor in order to improve nanowire-polymer interface and the sensor fabrication yield.

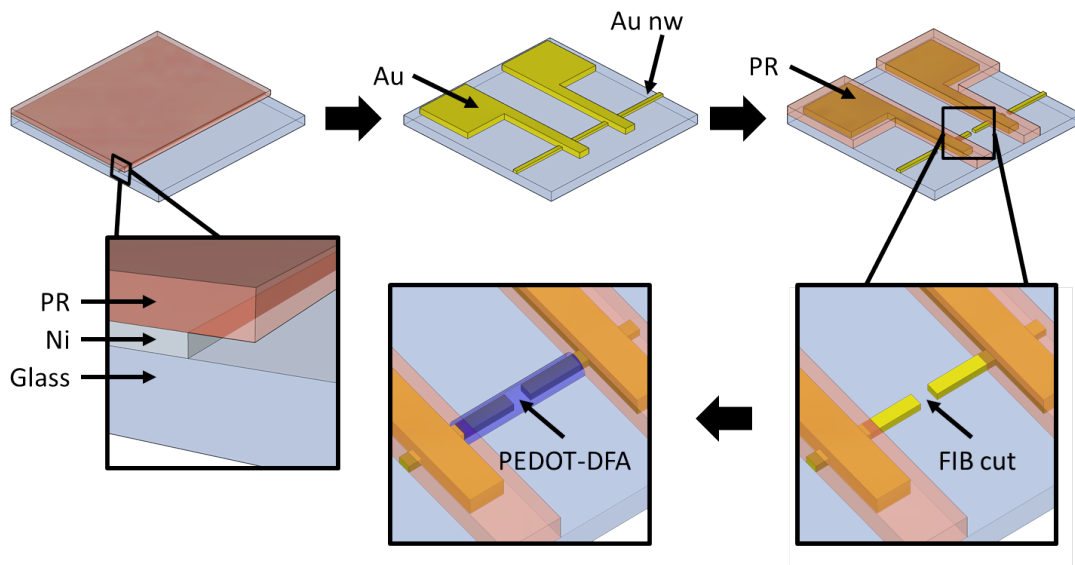


Figure 2.7: Process flow for fabrication of the core-shell PEDOT-DFA nanojunction.

2.3.2 PEDOT-DFA Core-shell Nanojunction

Following the challenges of the first-generation design of the chemiresistor, the next iteration needed to provide more open access to the nanogap. By scaling back the photoresist layer to protect only the contact pads, the bulk source of organic residues is far removed from the nanogap, and the nanowire can be easily observed optically to examine the effects of various cleaning methods or electrodeposition parameters. The revised process flow is shown in Figure 2.7. Rather than leaving a continuous photoresist layer on the slide before the FIB cut, the layer is patterned to only cover the contacts, leaving a large portion of the nanowire exposed. Because of this, the final step of electrodepositing the PEDOT-DFA not only fills in the nanogap, but also coats the length of the nanowire, making a core-shell structure. In principle, the core-shell structure is largely identical to the original embedded nanoreceptor: the resistivity of gold is nine orders less than that of PEDOT-DFA,⁴⁹ therefore the shell along the length of the nanowire does not participate in carrying any current. The PEDOT-DFA residing inside the nanogap remains the dominant actor in the system. Initially, these second generation devices used the same platinum nanowires as before, however the PEDOT-DFA

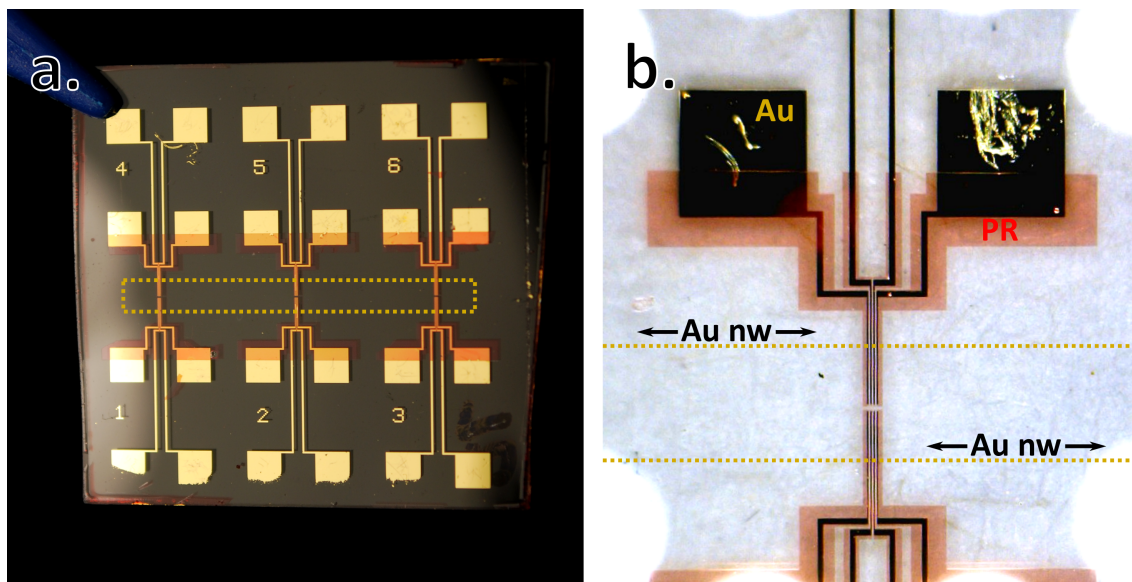


Figure 2.8: (a) Image of the completed slide containing up to eighteen core-shell nanojunction chemiresistors. (b) Magnified optical microscope image of the gold contacts and protective photoresist (PR) covering. The dotted yellow line indicates the gold nanowire in both images.

shells were prone to flaking off. Gold has been shown to have better adhesion and lower contact resistance with PEDOT,⁵⁶ so the switch was made to a gold nanowire core grown from a commercial solution (Clean Earth Solutions™) at -0.9 V vs. SCE for 1000 s in the LPNE template.

The new contacts are shown in Figure 2.8. Six identical sets of 4-point contacts, each electrode separated by $25\text{ }\mu\text{m}$, were patterned onto the slide using liftoff. Each 4-point contact can instead be treated as 3 sets of 2-point contacts, making a total of 18 nanowire segments of $25\text{ }\mu\text{m}$ length that are addressed. A final layer of photoresist is then patterned to cover the contacts, leaving a $16\text{ }\mu\text{m}$ length of gold nanowire exposed. A 100 nm gap is then cut in the center of each gap with a 30 kV , 1.5 pA FIB followed by 5 minutes of oxygen plasma cleaning. At this point, the gold nanowire surfaces were still fairly dirty, so the nanowires were cycled in $0.1\text{ M H}_2\text{SO}_4$ from $0.3 - 1.5$ V vs. SCE for at least 5 cycles, or until the reduction and oxidation peaks were visible. Typically, a gold electrode might be cycled until the redox peaks either plateau or start decreasing over time, however that point was never reached in this experiment; the peak currents kept increasing. Most likely, this

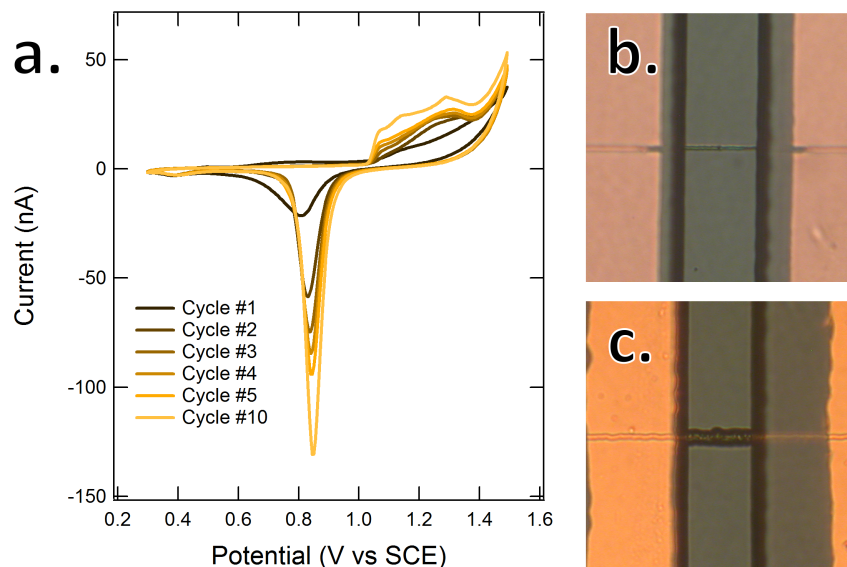


Figure 2.9: (a) Cyclic voltammetry of a gold nanowire in 0.1 M H_2SO_4 , scanning between 0.3-1.5 V vs. SCE at 20 mV/s. To the right are optical images of two nanojunctions where (b) was not and (c) was cycled in 0.1 M H_2SO_4 prior to electrodeposition of PEDOT-DFA under identical conditions.

indicates there was leakage through the photoresist and the gold contacts were contributing to the voltammetry. The voltammogram, shown in Figure 2.9a, matches those seen in earlier studies of LPNE gold nanowires and is characteristic of polycrystalline gold.⁵⁷ Figures 2.9b,c show the difference made by the H_2SO_4 cycling: under identical conditions for PEDOT-DFA electrodeposition, far more material is deposited on the cycled nanowire junction.

The pulsed deposition of PEDOT-DFA was changed in favor cyclic deposition to hew more closely to well-studied techniques and ease troubleshooting. PEDOT-DFA was deposited from the same solution as before in a single linear sweep from 0.4 to 1.1 V vs. SCE at 20 mV/s, sequentially depositing on one half of the junction at a time. Figure 2.10a shows the linear sweep voltammetry of one such deposition. Figures 2.10b,c show the nanowire nanogap before and after the electrodeposition. SEM images of the bare nanowire nanogap are in Figures 2.11a,b, and Figure 2.11c shows the completed core-shell nanojunction. This particular nanojunction will be referred to as sensor S1 in the next section. The resistance of the core-shell nanojunction chemiresistors was actually well below the expected

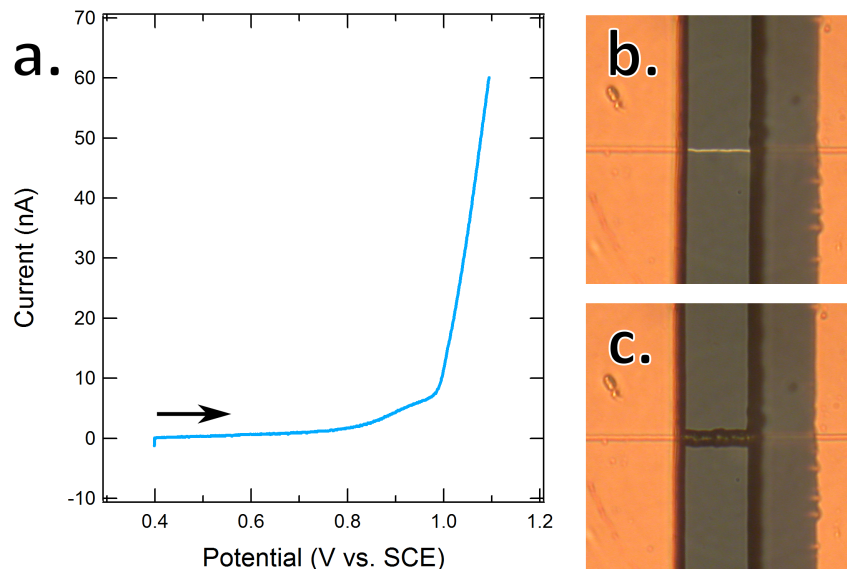


Figure 2.10: (a) Linear sweep voltammery of the electropolymerization of PEDOT-DFA on a single gold nanowire from 0.4 to 1.1 V vs. SCE at 20 mV/s. To the right are optical microscope images of a single nanowire nanogap (b) before and (c) after electropolymerization.

value, falling between 5 – 200 k Ω .

2.4 Fe(III) Detection by Core-shell Nanojunction

2.4.1 Fe(III) Sensing Experiment

Immediately following the deposition of PEDOT-DFA, the core-shell nanojunctions were equilibrated overnight in a solution of 0.1 M NaNO₃ and 5 mM HNO₃. The nanojunction sensors were then exposed by pipetting a 20 μ L droplet of the lowest concentration Zn(NO₃)₂, 0.1 M NaNO₃, 5 mM HNO₃ solution onto the nanowire and allowing it to equilibrate for 35 minutes. The droplet was replaced every 20 min with identical solution in order to maintain the concentration against evaporation. Five consecutive electrochemical impedance spectroscopy (EIS) measurements were taken (Gamry Series G 300) at 41 frequencies from 10 Hz to 100 kHz with a 10 mV rms amplitude centered at OCV. Five consecutive IV curves

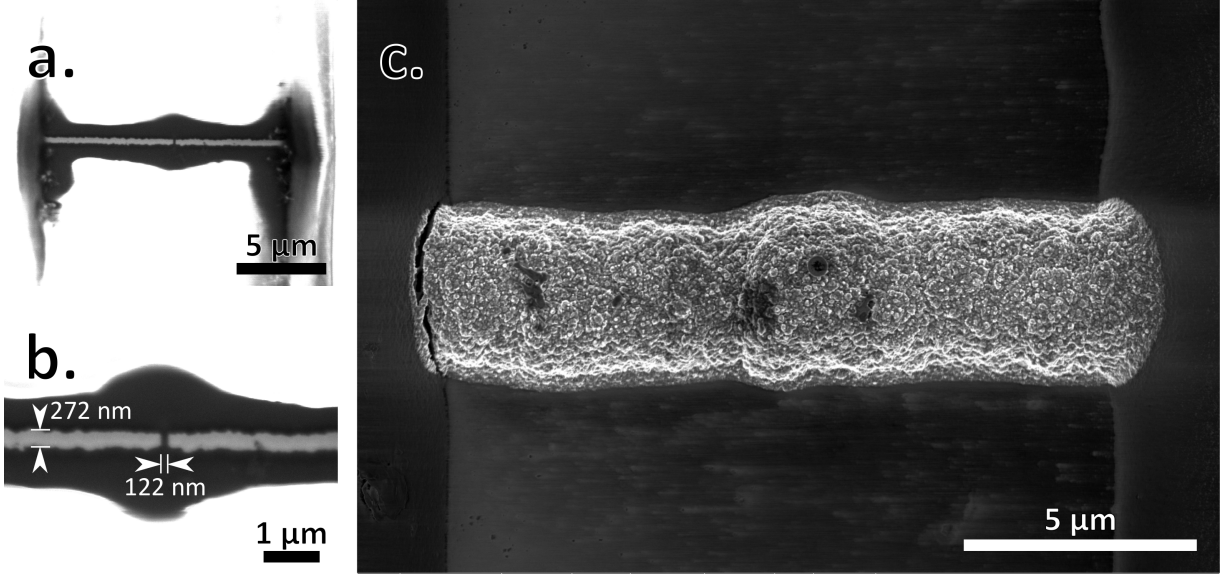


Figure 2.11: (a) SEM image of the bare gold nanowire just after the FIB cut was made. (b) Close-up of the 122 nm wide FIB cut in the 272 nm wide nanowire. (c) SEM of the core-shell nanojunction after PEDOT-DFA deposition.

were then measured by sweeping the potential difference across the nanogap from -20 mV to +20 mV at 10 mV/s. Following the measurements, the droplet was replaced and the process was repeated for the remaining concentrations of $\text{Zn}(\text{NO}_3)_2$, then for all concentrations of $\text{Fe}(\text{NO}_3)_3$, 0.1 M NaNO_3 , 5 mM HNO_3 solutions.

2.4.2 Results and Discussion

The results of two particular core-shell nanojunction chemiresistors will be examined in this section and are labeled as S1 ($R_0 = 13.5 \text{ k}\Omega$) and S2 ($R_0 = 17.1 \text{ k}\Omega$). The neighboring sensors were fabricated in the same bath under identical conditions. Figure 2.12 shows the Nyquist plots of S1 while equilibrated in the various concentrations of Zn(II) and Fe(III) droplets. In the presence of Zn(II), the impedance of the nanojunction drops from the initial, but there are no other clear correlations as the curves do not appear to have any dependence on the Zn(II) concentration. The behavior is far more ordered in Figure 2.12b, where the curves appear largely in order of Fe(III) concentration. A MATLAB script (Ap-

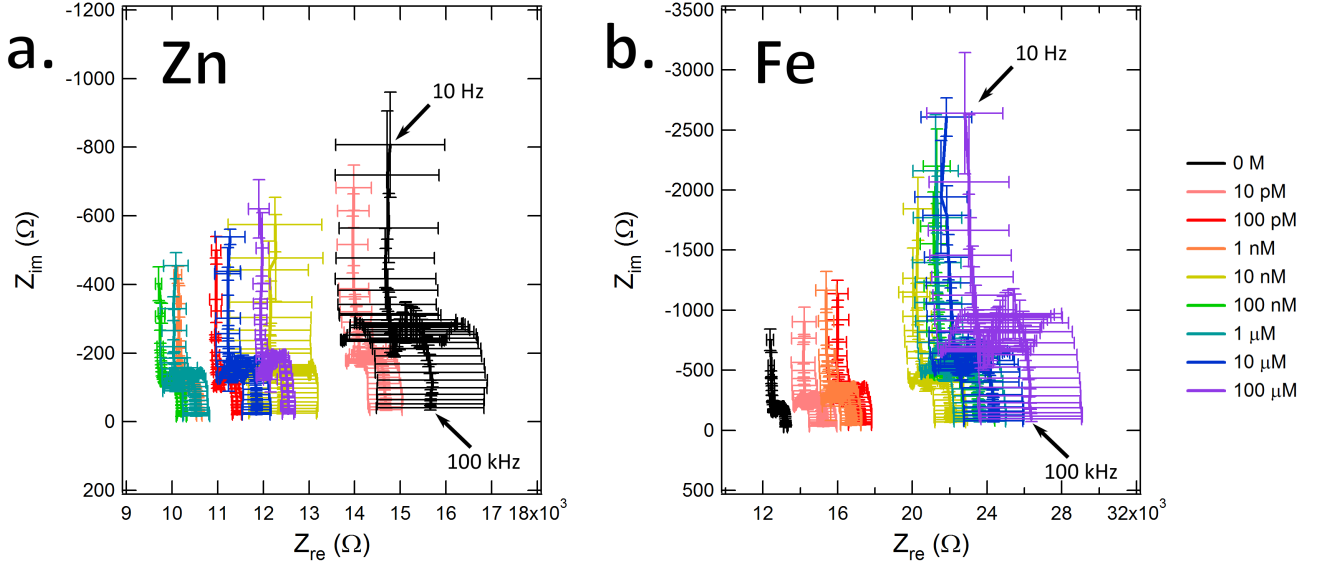


Figure 2.12: Nyquist plots showing the EIS response of sensor S1 to (a) Zn(II) and (b) Fe(III). All traces begin with 10 Hz near the top of the figure and follow to 100 kHz near the bottom. Error bars represent $\pm$ one standard deviation of five consecutive EIS measurements.

pendix B.1) was written to break down the data and examine the effects of the cations on real (Z_{re}) and imaginary (Z_{im}) impedance at each frequency measured. The changes in both real and imaginary impedance were found to linearly depend on the $\log[\text{Fe}^{3+}]$ across all frequencies. There does not appear to be any preferred frequency range for optimal performance: linear fits were made with the coefficient of determination $R^2 > 0.9$ for a majority of frequencies. The worst quality fit in the set was only $R^2 = 0.84$. Additionally, the signal-to-noise ratio (change in impedance divided by one standard deviation, $\Delta Z/\sigma$) was also constant for Z_{re} across the frequencies sampled. For Z_{im} , the signal-to-noise ratio was more favorable for $f < 1$ kHz. The complete set of these plots generated for S1 and S2 is available in Appendix B.2.

Figure 2.13 shows the normalized ΔZ_{re} and ΔZ_{im} as a function of cation concentration at one selected frequency, $f = 100$ Hz. As it seemed from the Nyquist plots, S1 and S2 are not sensitive to different concentrations of Zn(II). Beyond 10^{-11} M, the impedance changes plateau in both Z_{re} and Z_{im} , with the nanojunctions becoming both less resistive and more capacitive. As Fe(III) binds to the PEDOT-DFA, these trends are reversed, and,

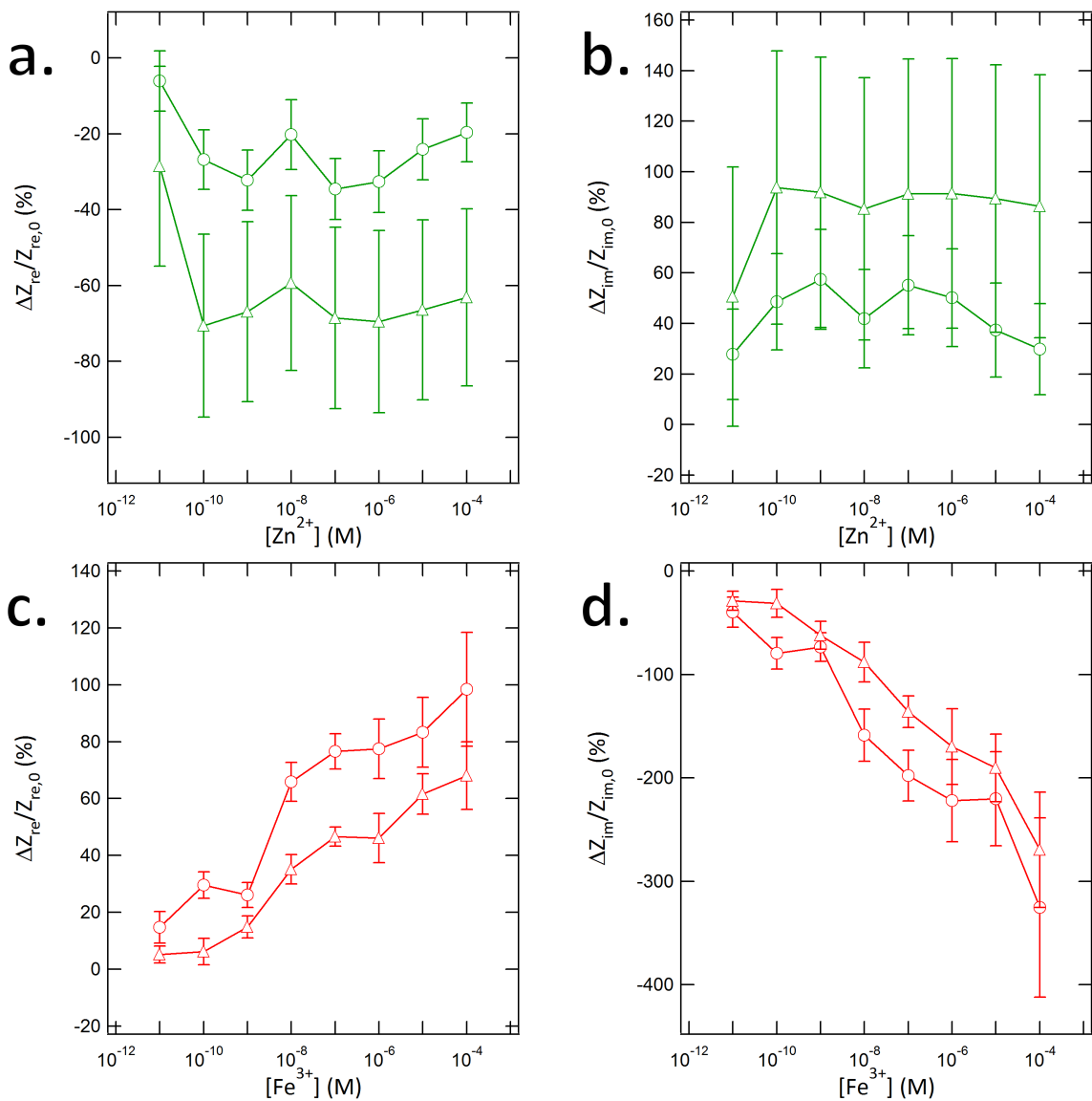


Figure 2.13: EIS response of sensors S1 (○) and S2 (△) at $f = 100$ Hz in the presence of (a,b) Zn(II) and (c,d) Fe(III). The response is shown as the normalized change in real (left) and imaginary (right) impedance from the initial measurement in background solution. Error bars represent $\pm$ one standard deviation of five consecutive EIS measurements.

as previously discussed, the linear relationship between the normalized change in impedance and $\log[\text{Fe}^{3+}]$ is seen clearly in Figure 2.13c,d. Figure 2.14 summarizes the DC electrical characterization of the sensors. The IV measurements show Ohmic behavior, which can be expected of a metal-semiconductor-metal junction in such a small potential window of $\Delta V = 40$ mV. The resistance data mirrors the behavior seen earlier in Z_{re} : resistance appears independent of $[\text{Zn}^{2+}]$, but linearly increases along with $\log[\text{Fe}^{3+}]$, and to nearly identical values as Z_{re} with either cation.

Despite using the same PEDOT-DFA transduction medium as Kindra *et al.*, there are several clear differences in the behavior of the nanowire array and the core-shell nanojunction presented here. The core-shell nanojunction is more sensitive to Fe(III) than the nanowire array, experiencing $\Delta R/R_0$ of 2-3 times greater magnitude. However, the response of the nanojunction is the opposite, becoming less conductive when binding Fe(III). Zn(II) provides some unusual discrepancies as well: though both chemiresistors become more conductive in Zn(II) solution, the response by the nanojunction is much larger and, for sensor S2, nearly the same magnitude as the signal from Fe(III). The initial equilibration is also notable, taking at least six hours to reach a stable baseline resistance (Figure 2.15), and then needing 35 minutes of equilibration in the analyte solutions. Unfortunately, despite the design choices made to decrease the sensing response time, that goal was not met. As seen in Figure 2.11, the PEDOT-DFA shell is a cylinder with a diameter of $3.5\ \mu\text{m}$, while the nanowires used by Kindra *et al.* had a rectangular cross section with a minimum dimension in the nanowire height of only 50 nm. Given the large resistivity of the material, this presents a much larger barrier to rapid mass transport within the core-shell nanojunction. That being said, the nanojunctions were still much more conductive than expected, which implies that the DFA-doping level may have been much lower than in Kindra's nanowire arrays. Many attempts were made to fabricate additional core-shell nanojunctions to confirm the above results and optimize the PEDOT-DFA shell thickness, but none were successful. Most of the attempts failed during the H_2SO_4 cycling: gold nanowires would be nearly entire dissolved

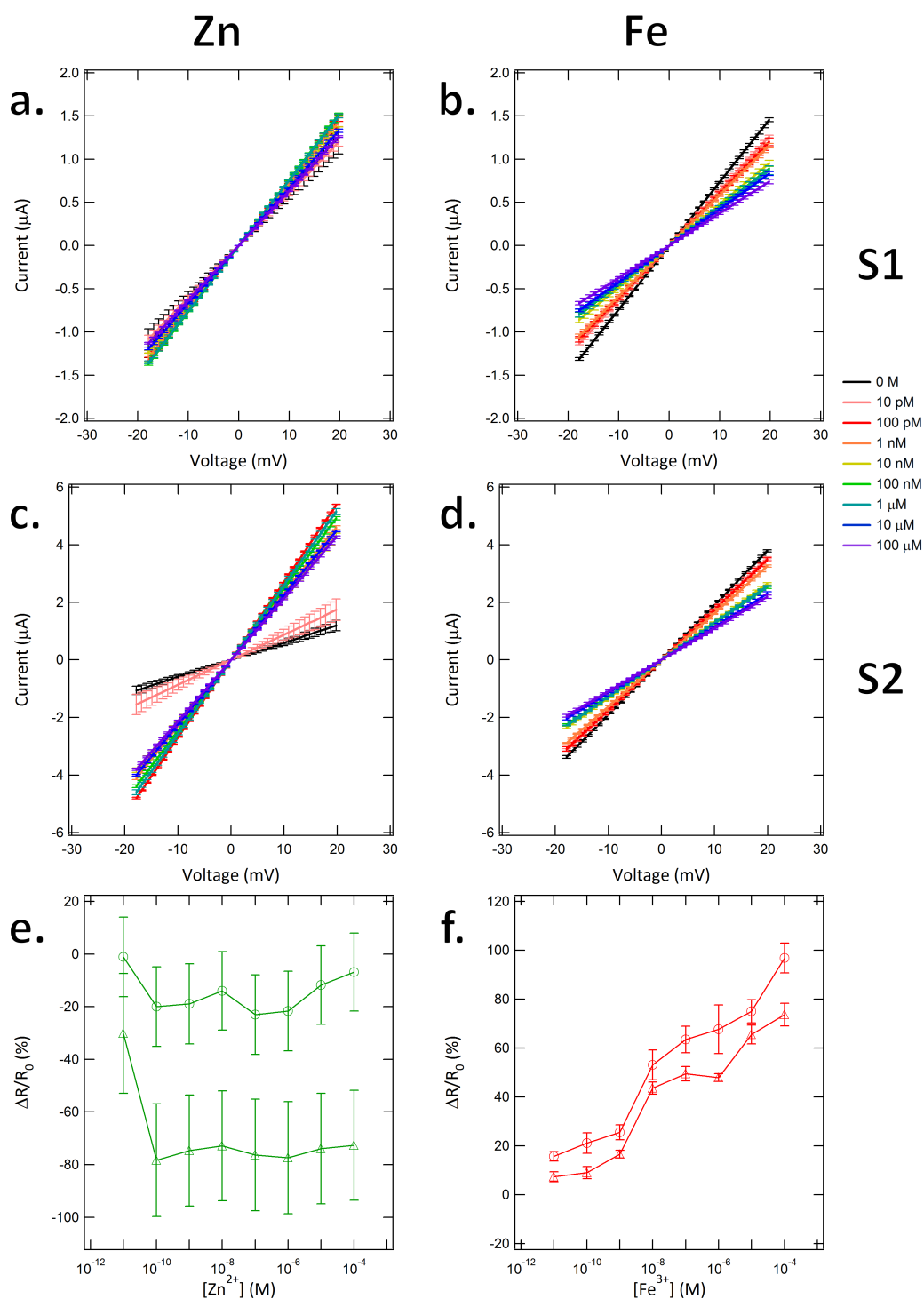


Figure 2.14: (a-d) IV measurements of sensors S1 (top row) and S2 (middle row) in response to 10^{-11} M - 10^{-4} M Zn(II) (left) and Fe(III) (right). Potential was swept from -20 mV to +20 mV at 10 mV/s. (e,f) Normalized change in resistance of S1 (○) and S2 (△) in (e) Zn(II) and (f) Fe(III) from the initial measurement in background solution. Error bars represent $\pm$ one standard deviation of five consecutive IV measurements.

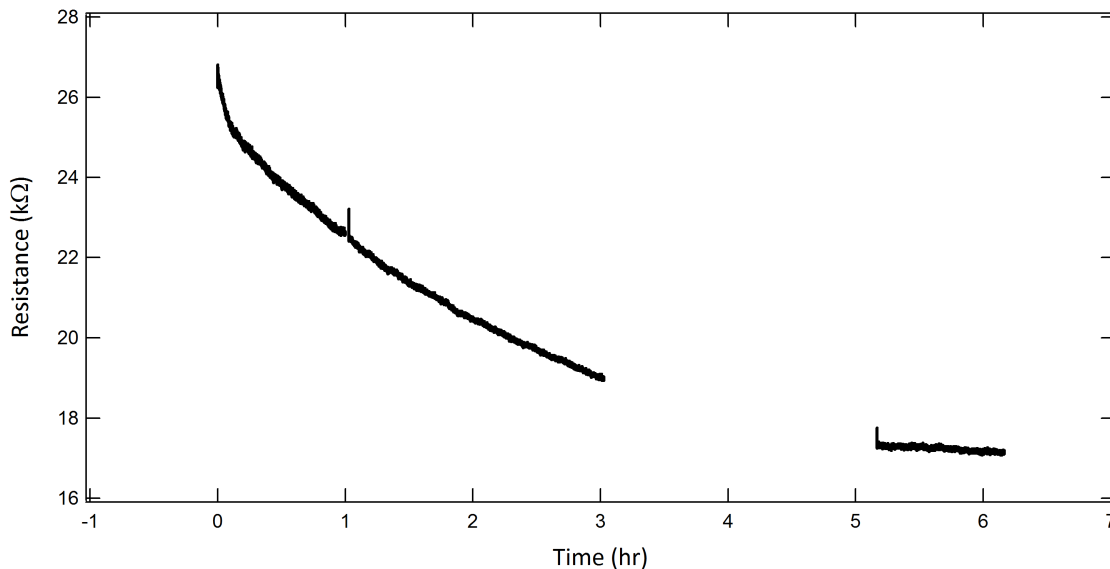


Figure 2.15: Resistance vs. time graph for a freshly made core-shell nanojunction sitting in 0.1 M NaNO_3 , 5 mM HNO_3 .

under the same conditions that left others optically unchanged and primed for PEDOT-DFA electrodeposition (Figure 2.16a). Many of the surviving nanowires were then host to very heterogeneous PEDOT-DFA coatings (Figure 2.16b), most likely due to residues remaining on the nanowires despite cleaning. Finally, those that were homogeneously coated with PEDOT-DFA and electrically reconnected fell apart during the sensing experiment, losing pieces of PEDOT-DFA and delaminating from the gold nanowire (Figure 2.16c,d).

A third generation sensor was made to try to solve the continued frustrations and inconsistencies along the interface between the metal nanowire core and the PEDOT-DFA layer. This time, the final photoresist layer that had been blocking off the contacts was omitted entirely. Doing this eliminates the largest source of organic residues that foul the nanowire surface and prove difficult to remove. Just before the PEDOT-DFA deposition, the slide was cleaned in piranha solution (3:1 H_2SO_4 : H_2O_2) for 20 minutes to eliminate any organic residues. This thorough cleaning enabled the thinnest, most homogeneous electrodepositions of PEDOT-DFA seen in this study, shown in Figure 2.17a, and dramatically improved the fabrication yield of nanojunctions. However, these nanojunctions show consistently poor

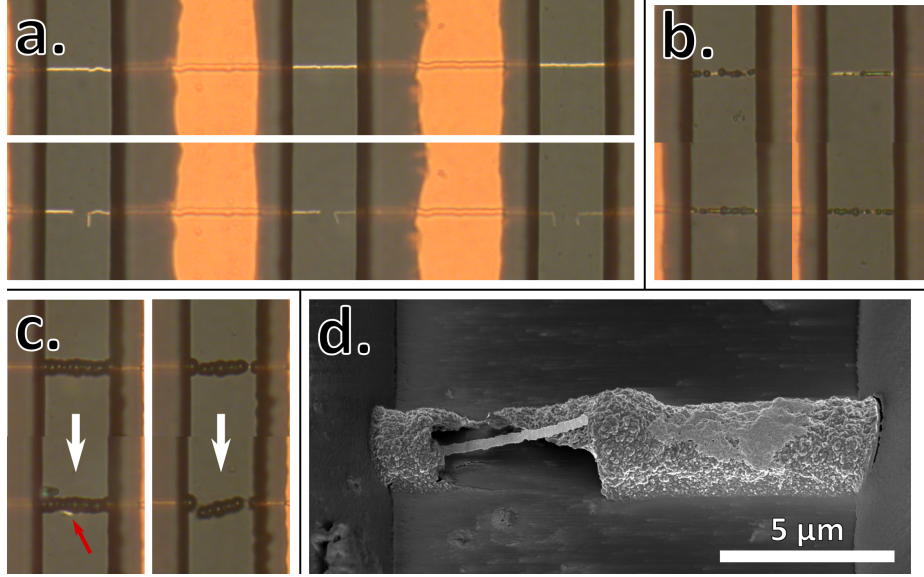


Figure 2.16: (a) Gold nanowires before (top) and after (bottom) cycling in H_2SO_4 . (b) Four examples of heterogeneous PEDOT-DFA deposition despite cleaning steps. (c) Failure of two junctions during the sensing experiment. On the left, the gold nanowire core (red arrow) becomes separated from the polymer. On the right, the PEDOT-DFA layer is twisting off of the gold nanowire. (d) SEM of a nanojunction after a large amount of the polymer layer is lost, exposing the gold nanowire on that side. Electron beam is tilted 45° from orthogonal.

sensing response (Figure 2.17b) with a normalized change in resistance an order of magnitude lower than the second generation sensors S1 and S2. It is not clear why the above changes led to such a falloff in performance, but it is possible the contact pads, now coated in PEDOT-DFA, bind a large share of the Fe(III) without affecting the resistance of the sensor.

2.5 Conclusion

Doped PEDOT nanojunction chemiresistors were fabricated on the backbone of a single metal nanowire for the fast, sensitive, and selective detection of Fe(III) in solution. Fabrication challenges, centered around the organic residues and the adhesion between the metal nanowire core and the PEDOT-DFA transduction layer, led to three design iterations of the sensor. The second generation sensor, the core-shell nanojunction with covered contacts,

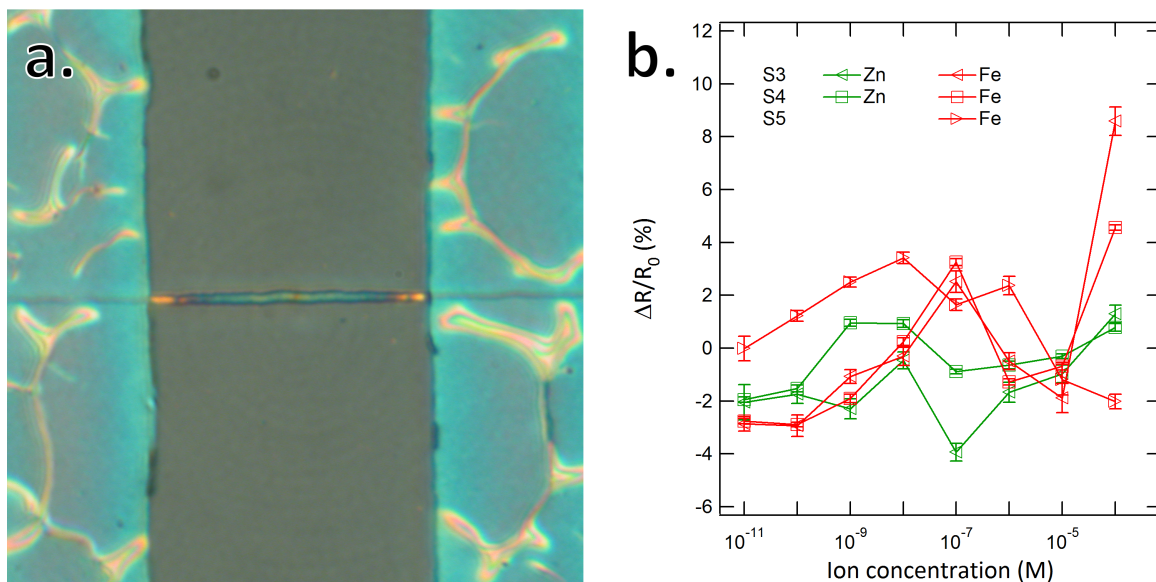


Figure 2.17: (a) Optical microscope image of the third generation core-shell nanojunction sensor. (b) Normalized change in resistance of three sensors in response to Zn(II) and Fe(III).

showed the most potential, detecting $10^{-11} - 10^{-4}$ M Fe(III), a dynamic range on par with and a limit of detection better than ISEs. The selectivity was less impressive, as Zn(II) also generated a large response from the sensor. The response time also did not improve on that of the PEDOT-DFA nanowire array, most likely due to the thick ($1.75 \mu\text{m}$) PEDOT-DFA transduction layer. The third generation sensor, seemingly having solved the issue of PEDOT-DFA adhesion, took a step backwards in sensitivity to Fe(III). Both of these designs also had much lower than expected resistances, possibly indicating a lower dopant concentration than the nanowire array of Kindra *et al.*.

Further studies on this system must find a means of effectively cleaning the nanowire surface for successful PEDOT-DFA deposition while blocking off the contact pads from absorbing the metal ion analyte. Different photoresists may be investigated for how cleanly they are removed during development, or the contacts may be protected by an inorganic insulator like Al_2O_3 . Following this, the electrodeposition of PEDOT-DFA on the nanojunction merits further review to understand whether the junction is sufficiently doped, to determine the optimum concentration of DFA in the plating solution, and to find the best

PEDOT-DFA shell thickness for Fe(III) sensing. Finally, with its metal-semiconductor-metal nanojunction, this chemiresistor is a prime candidate for conversion to a FET. The nanojunction conductivity could be modulated with the addition of a back gate or a solution gate, and investigated for any possible enhancement in sensitivity, selectivity, or speed of detection.

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Appendix A

Gold Nanowire Thermophones

A.1 Amplifier Design

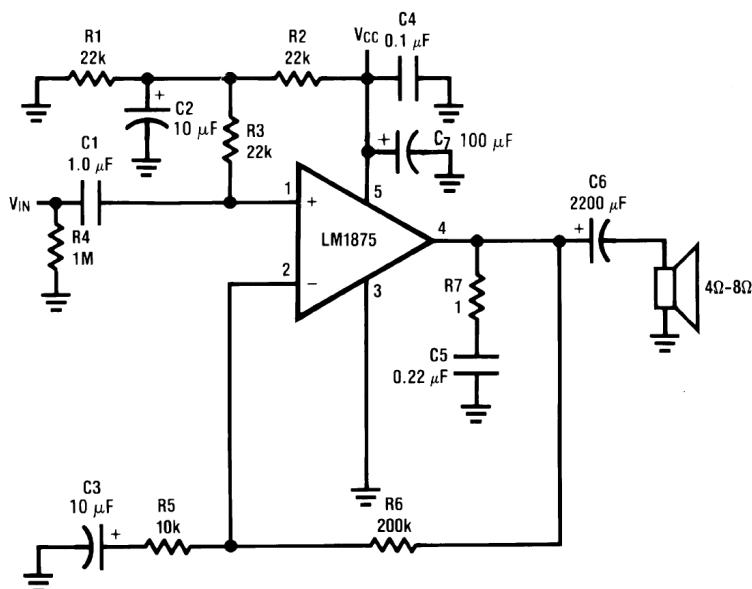


Figure A.1: Circuit diagram for the amplifier used in this experiment provided by Texas Instruments: <http://www.ti.com.cn/cn/lit/ds/symlink/lm1875.pdf>

A.2 Substrate Overheating

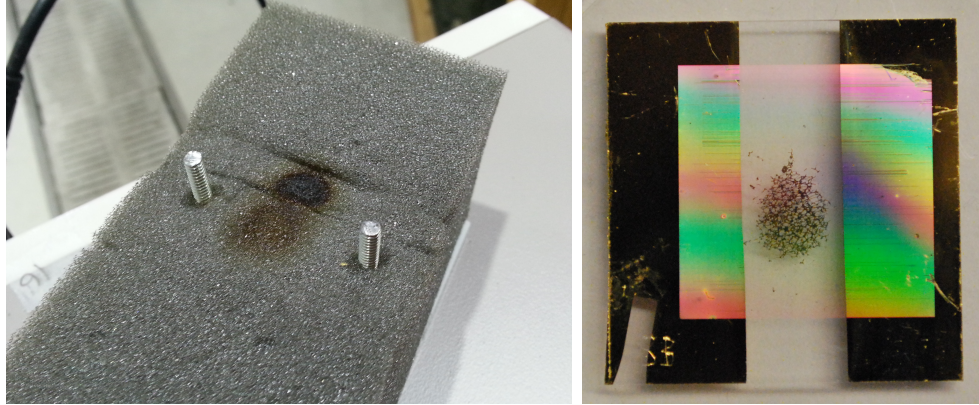


Figure A.2: (l) Burn marks on the sample stage after running several gold nanowire thermophones at $P_{in} = 2.5$ W. (r) Optical image of a gold nanowire thermophone after 2.5 W operation. Note the dark spot at the center, where acoustical foam has adhered to the back of the slide due to high temperatures in the glass substrate.

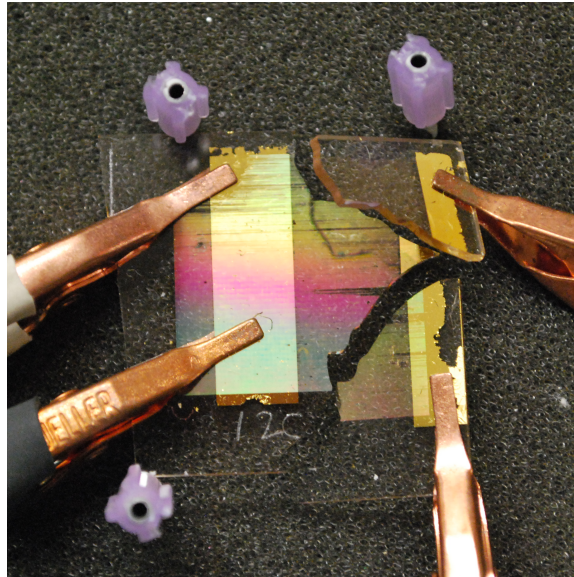


Figure A.3: Optical image of a shattered gold nanowire thermophone. Increasing the input power too quickly would often cause this.

A.3 Constants Used in Calculation

Variable	Parameter	Value
κ	thermal conductivity of air	2.63×10^{-2} W/m K
ρ_0	density of air	1.16 kg/m ³
α	thermal diffusivity of air	2.25×10^{-5} m ² /s
T_0	temperature of air	300 K
C_s	heat capacity per unit area	$\rho_{Au}v_{nw}C_{Au}N/A$
ρ_{Au}	density of gold	1.93×10^4 kg/m ³
C_{Au}	heat capacity of gold	129.1 J/kg K
v_{nw}	volume of a single nanowire	7 mm $\times$ 100 nm $\times w$
N	number of nanowires	4000 wires
A	thermophone area	1.4×10^{-4} m ²
α_{sub}	thermal diffusivity of glass	4.69×10^{-7} m ² /s
C_{sub}	heat capacity of glass	705 J/kg K
γ	heat capacity ratio of air	1.4
v_g	speed of sound in air	343.2 m/s
e_s	thermal effusivity of glass	$\sqrt{\kappa_s \rho_s C_{sub}}$
κ_s	thermal conductivity of glass	0.86 W/m K
ρ_s	density of glass	2.6×10^3 kg/m ³
e_g	thermal effusivity of air	$\sqrt{\kappa \rho_0 C_g}$
C_g	heat capacity of air	1007 J/kg K

Appendix B

Doped PEDOT Chemiresistor

B.1 MATLAB Code

B.1.1 EIS

```
function ionsensing(folder,ion,lowC,highC)
%(folder name, element, log low conc, log high conc)
%Place all data in subfolder named Impedance

sensors = dir([folder '\Impedance\']);
conc = [0 lowC:highC];

%start data analysis
for i = 1:length(sensors)

%collect signals vs ion concentration and do stats
for k = 1:length(conc);
for j = 1:5 %# of repeated measurements
data = dlmread([folder '\Impedance\' sensors(i+2).name '\' ion '-EIS(' int2str(conc(k)) '
)_' int2str(j) '.DTA'], '\t',43,0);
var1(:,j) = data(:,4);%Zre
var2(:,j) = data(:,5);%Zim
end
avgZre(:,k) = mean(var1,2);
avgZim(:,k) = mean(var2,2);
stdZre(:,k) = std(var1,[],2);
stdZim(:,k) = std(var2,[],2);
end
freq = data(:,3);
clear('var1','var2')
```

```

for j = 2:length(conc)
%calc deltaZ and std
delZre(:,j-1) = avgZre(:,j) - avgZre(:,1);
stdZre(:,j-1) = (stdZre(:,1).^2 + stdZre(:,j).^2).^(1/2);
delZim(:,j-1) = avgZim(:,j) - avgZim(:,1);
stdZim(:,j-1) = (stdZim(:,1).^2 + stdZim(:,j).^2).^(1/2);
end

for j = 1:length(delZre(1,:))
%calc normalized delZ and std
normZre(:,j) = delZre(:,j)./abs(avgZre(:,1));
nstdZre(:,j) = normZre(:,j) .* sqrt((stdZre(:,j) ./ delZre(:,j)) .^ 2 + (stdZre(:,1)
./ avgZre(:,1)) .^ 2);
normZim(:,j) = delZim(:,j)./abs(avgZim(:,1));
nstdZim(:,j) = normZim(:,j) .* sqrt((stdZim(:,j) ./ delZim(:,j)) .^ 2 + (stdZim(:,1)
./ avgZim(:,1)) .^ 2);
end

%calc signal-to-noise
SNRZre = abs(delZre ./ stdZre);
SNRZim = abs(delZim ./ stdZim);

%write EIS output
dlmwrite([folder '\ sensors(i+2).name '.' ion '.txt'],[freq avgZre stdZre avgZim stdZim
delZre stdZre delZim stdZim normZre nstdZre normZim nstdZim SNRZre SNRZim],'\t'
);

%freq vs. concentration
TnormZre = transpose(normZre);
TnormZim = transpose(normZim);
TnstdZre = transpose(nstdZre);
TnstdZim = transpose(nstdZim);
C = transpose(conc(2:end));

%fit to linear model, store R^2 values
X = [ones(length(C),1) C];

for j = 1:41
Yre = TnormZre(:,j);
Yim = TnormZim(:,j);
Bre(:,j) = X\Yre;
Bim(:,j) = X\Yim;
R2NZre(j,1) = 1 - sum((Yre - X*Bre(:,j)).^2)/sum((Yre - mean(Yre)).^2);
R2NZim(j,1) = 1 - sum((Yim - X*Bim(:,j)).^2)/sum((Yim - mean(Yim)).^2);
end

%write conc depedant output
dlmwrite([folder '\ sensors(i+2).name '_conc' ion '.txt'],[C TnormZre TnormZim TnstdZre
TnstdZim],'\t');
dlmwrite([folder '\ sensors(i+2).name '_R2' ion '.txt'],[freq R2NZre R2NZim],'\t');
dlmwrite([folder '\ sensors(i+2).name '_fit' ion '.txt'],[Bre Bim],'\t');

[Remax,inre] = max(R2NZre);
[Immax,inim] = max(R2NZim);

figure('Name',sensors(i+2).name)
subplot(3,2,1)
semilogx(freq,R2NZre)

```

```

axis([1 10^6 0 1])
title(['Z_{re}, max R^{2} = ' sprintf('%.3f',Remax)])
ylabel('R^{2}')
xlabel('Frequency (Hz)')

subplot(3,2,2)
semilogx(freq,R2NZim)
axis([1 10^6 0 1])
title(['Z_{im}, max R^{2} = ' sprintf('%.3f',Immax)])
ylabel('R^{2}')
xlabel('Frequency (Hz)')

subplot(3,2,3)
errorbar(C,100*TnormZre(:,inre),100*TnstdZre(:,inre),'.k')
hold on
plot(C,X*Bre(:,inre)*100,'--')
title(['f = ' int2str(freq(inre)) ' Hz'])
xlabel(['log(' ion ')'])
ylabel(['\Delta' 'Z_{re}/Z_{re0}, %'])
grid on

subplot(3,2,4)
errorbar(C,100*TnormZim(:,inim),100*TnstdZim(:,inim),'.k')
hold on
plot(C,X*Bim(:,inim)*100,'--')
title(['f = ' int2str(freq(inim)) ' Hz'])
xlabel(['log(' ion ')'])
ylabel(['\Delta' 'Z_{im}/Z_{im0}, %'])
grid on

subplot(3,2,5)
semilogx(freq,SNRZre)
axis([1 10^6])
title(['Signal-to-noise ' '\Delta' 'Z_{re}'])
ylabel(['\Delta' 'Z_{re}/' '\sigma'])
xlabel('Frequency (Hz)')

subplot(3,2,6)
semilogx(freq,SNRZim)
axis([1 10^6])
title(['Signal-to-noise ' '\Delta' 'Z_{im}'])
ylabel(['\Delta' 'Z_{im}/' '\sigma'])
xlabel('Frequency (Hz)')

end

```

B.1.2 DC

```

function ionsensingDC(folder,ion,lowC,highC)
%(folder name, log low conc, log high conc)
%Place all data in subfolder named Impedance

sensors = dir([folder '\Impedance\']);
conc = [0 lowC:highC];

```

```

%start data analysis
for i = 1:length(sensors)
for c = 1:length(conc)
%collect signals vs ion concentration and do stats
for j = 1:5
bckd = dlmread([folder '\Impedance\' sensors(i+2).name '\ ion '-sweep(' int2str(conc(c))
    '_#' int2str(j) '.DTA'], '\t',50,0);
var1(:,j) = bckd(3:end,4);%I
if (c==1)
if (j==1)
volt = bckd(3:end,3);%set master V
endif
endif
var2(:,j) = bckd(3:end,3);%V
var3(:,j) = [ones(length(var2(:,j)),1) var2(:,j)]\var1(:,j);
end
%Small discrepancies in V require interpolation to match c=j=1 set (volt)
n = length(volt);
for j = 1:5
if (var1(1,j) < volt(1))
curr(1,j) = var1(1,j)+(volt(1)-var2(1,j))*(var1(2,j)-var1(1,j))/(var2(2,j)-var2(1,j));
for k = 2:n
curr(k,j) = var1(k,j)+(volt(k)-var2(k,j))*(var1(k+1,j)-var1(k,j))/(var2(k+1,j)-var2(k,j))
;
end
else
for k = 1:(n-1)
curr(k,j) = var1(k,j)+(volt(k)-var2(k,j))*(var1(k+1,j)-var1(k,j))/(var2(k+1,j)-var2(k,j))
;
end
curr(n,j) = var1(n-1,j)+(volt(n)-var2(n-1,j))*(var1(n,j)-var1(n-1,j))/(var2(n,j)-var2(n-1,j));
endif
end
avgI(:,c) = mean(curr,2);
stdI(:,c) = std(curr,[],2);
avgR(c,:) = mean(var3(2,:).^(-1),2);
stdR(c,:) = std(var3(2,:).^(-1),[],2);
offR(c,:) = mean(var3(1,:),2);
if (c>1)
delR(c-1,:) = avgR(c,:)-avgR(1,:);
stdR(c-1,:) = (stdR(c,:).^2 + stdR(1,:).^2).^(1/2);
normR(c-1,:) = delR(c-1,:)/avgR(1,:);
NstdR(c-1,:) = normR(c-1,:).*((stdR(c-1,:)./delR(c-1,:)).^2 + (stdR(1,:)./avgR(1,:)).^2)
.^(1/2);
endif
end

clear('var1','var2','var3')

%write IV output
dlmwrite([folder '\ sensors(i+2).name '_IV.' ion '.txt'],[volt avgI stdI],'\t');

%R vs. concentration
C = transpose(conc);

dlmwrite([folder '\ sensors(i+2).name '_resist.' ion '.txt'],[C avgR stdR],'\t');

```

```

dlmwrite([folder '\' sensors(i+2).name '_normR.' ion '.txt'],[C(2:end) delR stddR normR
NstdR],'\t');

colors = [0 0 0; 0.5 0 0; 1 0 0; 1 0.5 0; 1 1 0; 0 1 0; 0 1 0.5; 0 0 1; 0.5 0 1];

figure('Name',sensors(i+2).name)
subplot(1,2,1)
for j = 1:length(conc)
scatter(volt,10^6*(avgI(:,j)-offR(j)),[],colors(j,:), "filled")
hold on
errorbar(volt,10^6*(avgI(:,j)-offR(j)),10^6*stdI(:,j),'k')
%hold on
end
title(sensors(i+2).name)
xlabel('Voltage□(V)')
ylabel(['Current□(' '\mu' 'A)'])

subplot(1,2,2)
errorbar(C(2:end),normR*100,NstdR*100,'.k')
title(['R_{0}□=□' int2str(avgR(1,:)) '□' '\Omega'])
ylabel(['\Delta' 'R/R_{0}□%'])
xlabel(['log([' ion '])'])

end

```

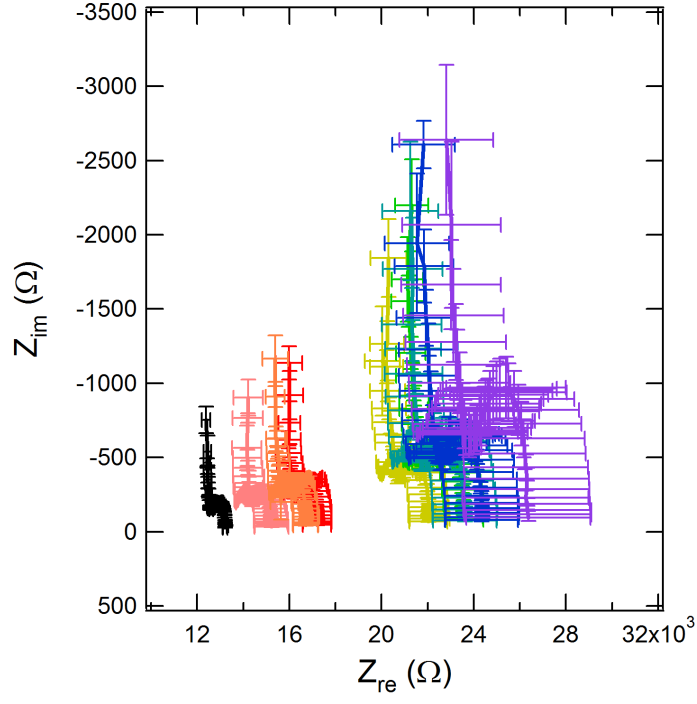
B.2 Complete EIS Data for S1 and S2

Legends:

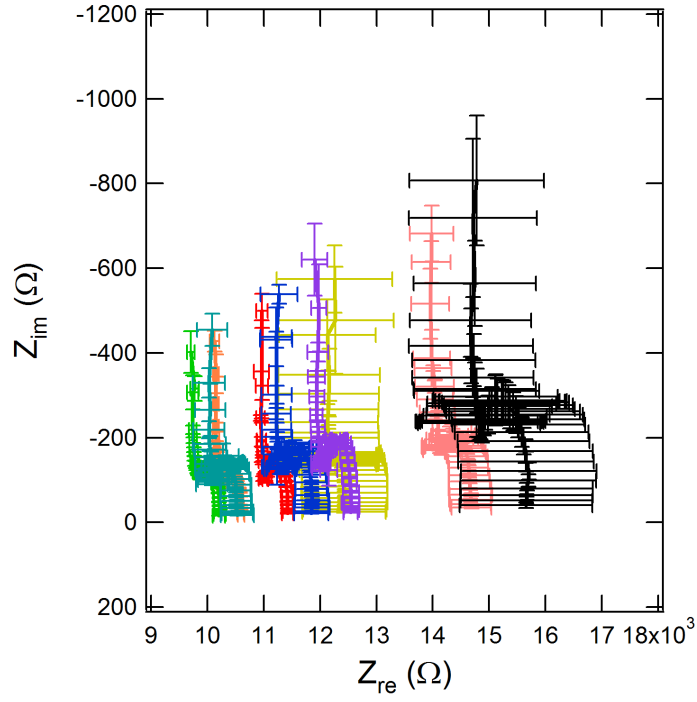
— 0 M	○ 0 M
— 10 pM	○ 10 pM
— 100 pM	○ 100 pM
— 1 nM	○ 1 nM
— 10 nM	○ 10 nM
— 100 nM	○ 100 nM
— 1 μ M	○ 1 μ M
— 10 μ M	○ 10 μ M
— 100 μ M	○ 100 μ M

B.2.1 S1

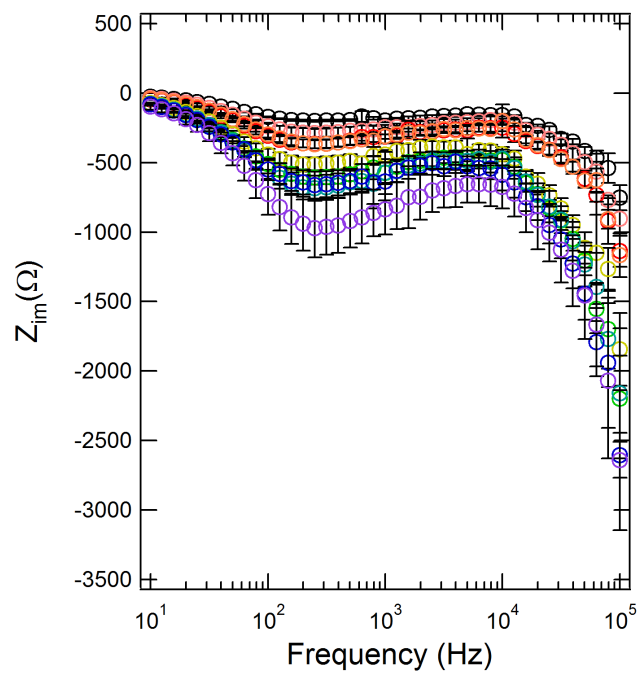
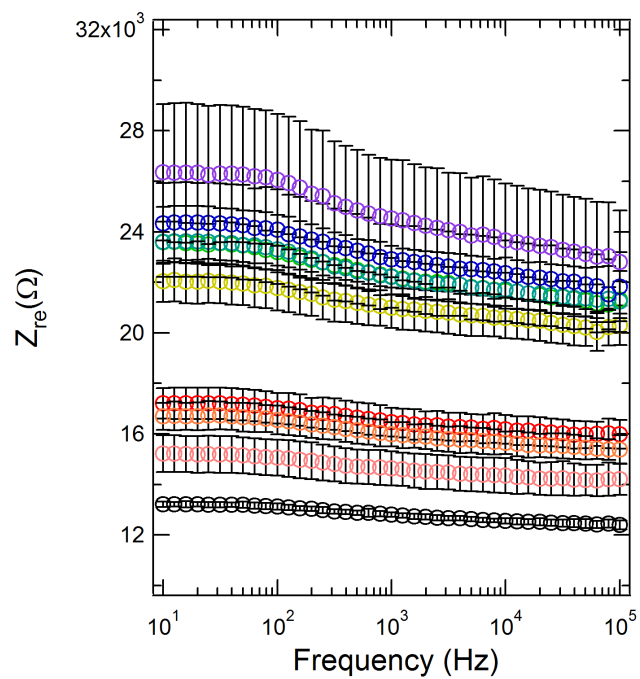
Fe(III)



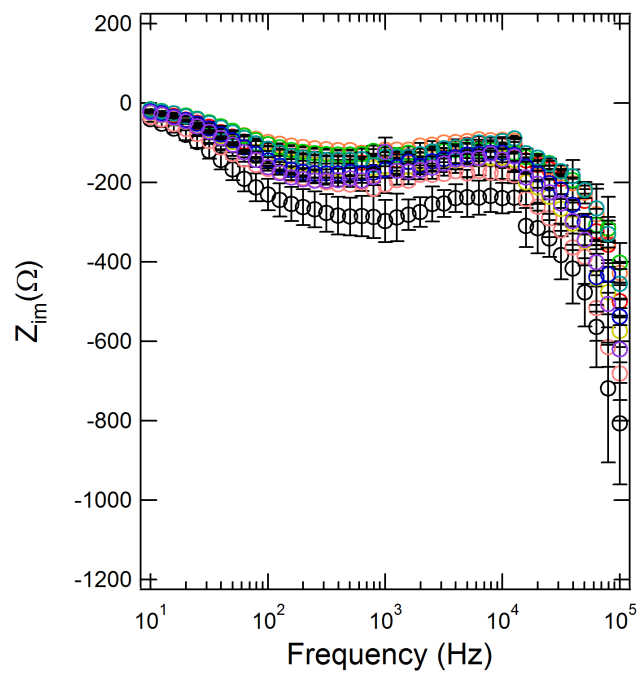
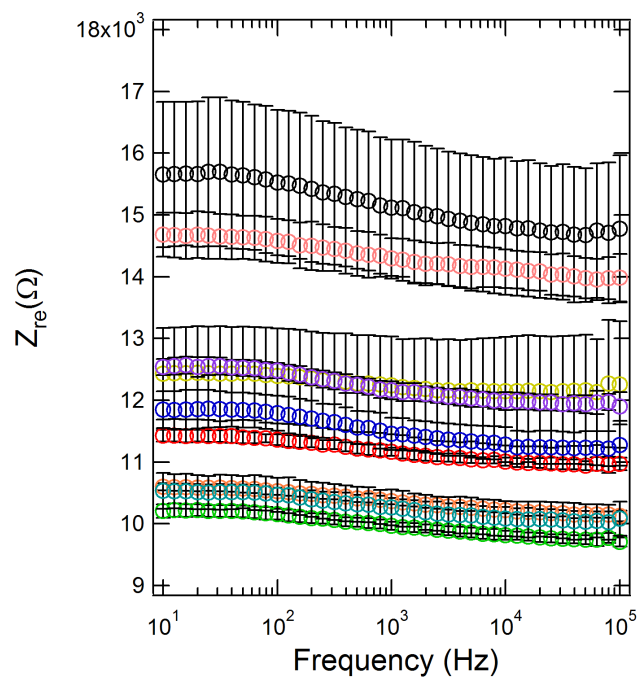
Zn(II)



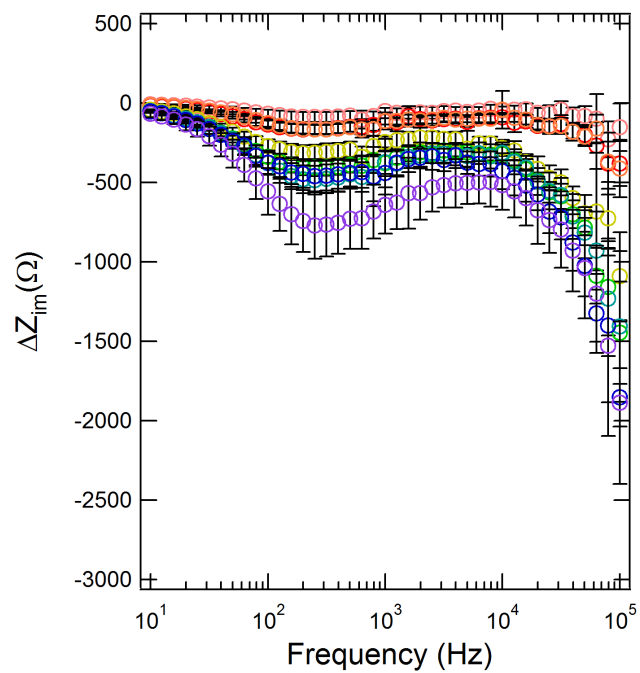
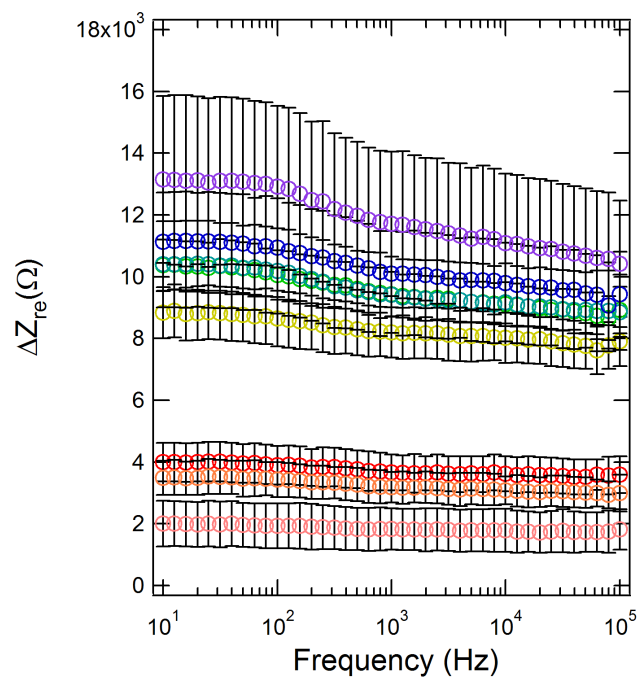
Fe(III)



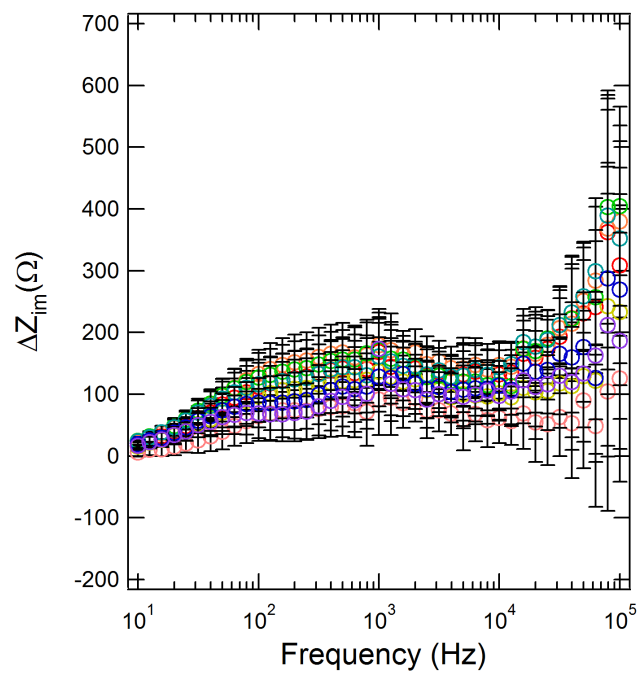
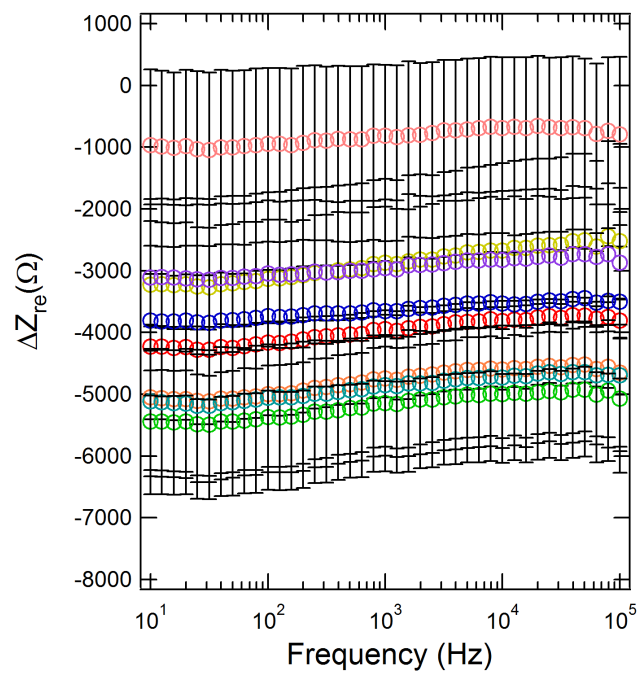
Zn(II)



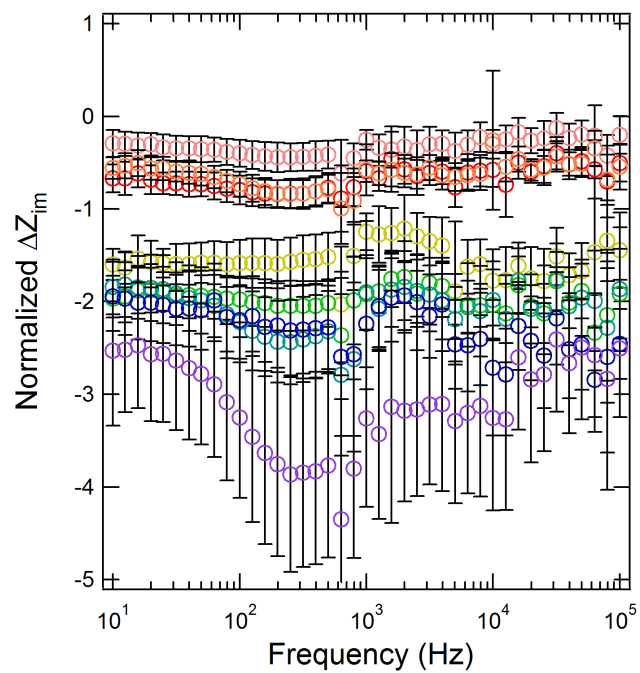
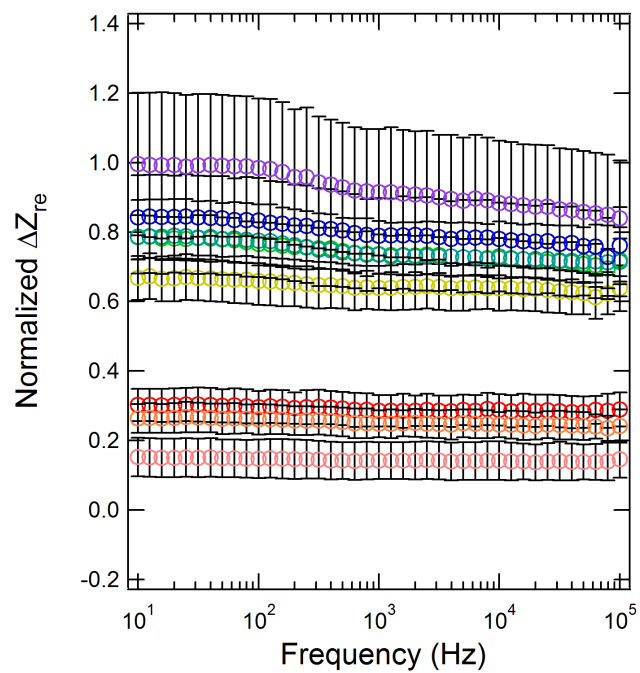
Fe(III)



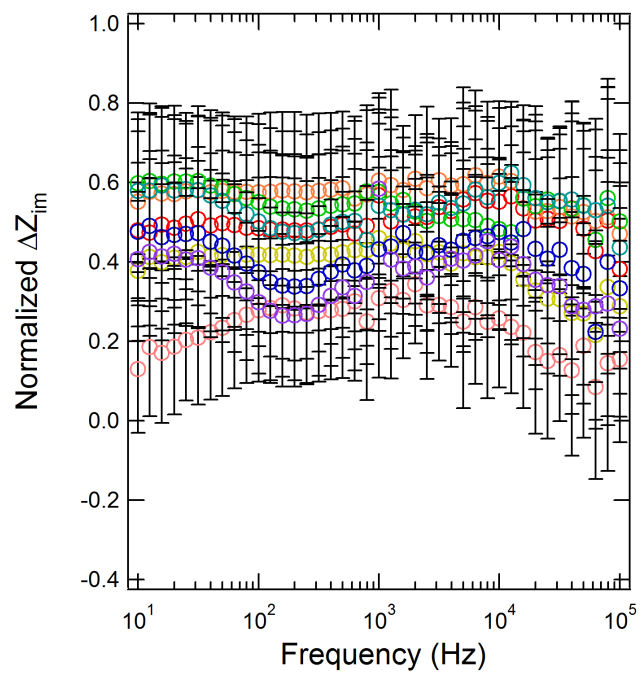
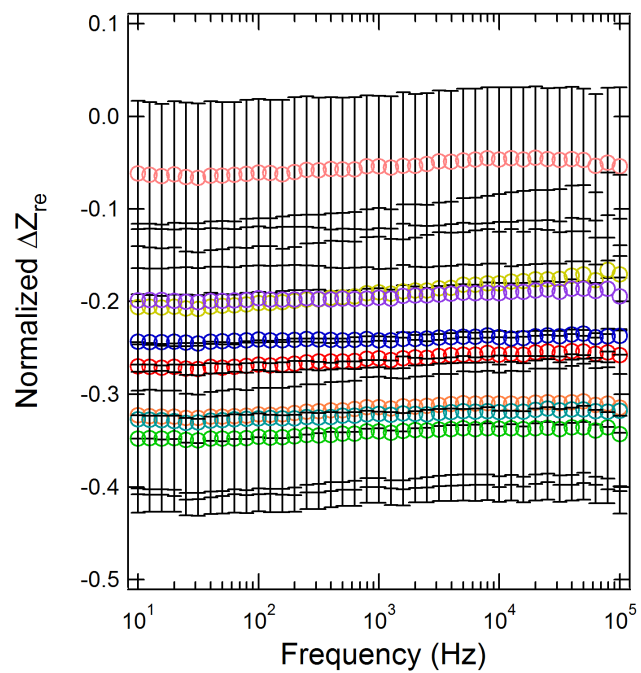
Zn(II)



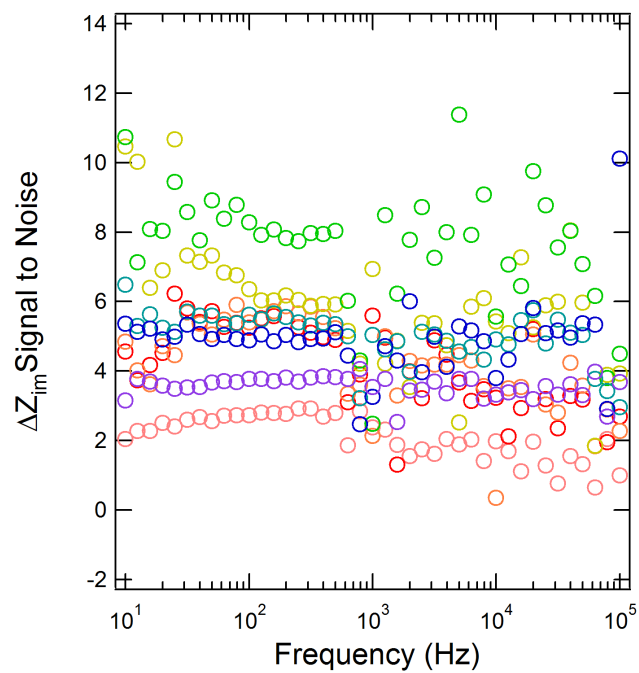
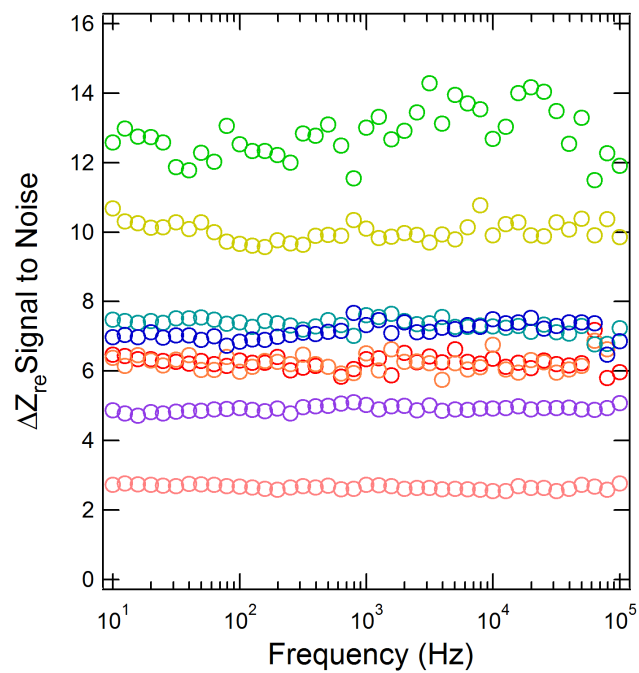
Fe(III)



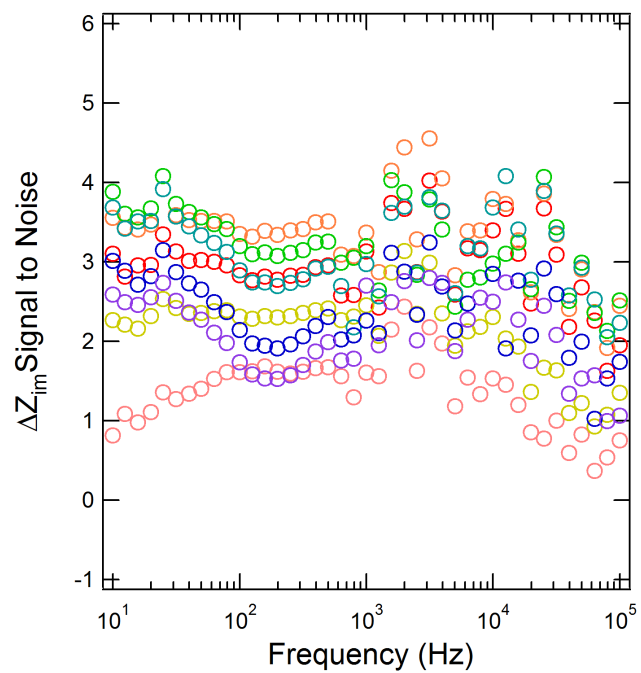
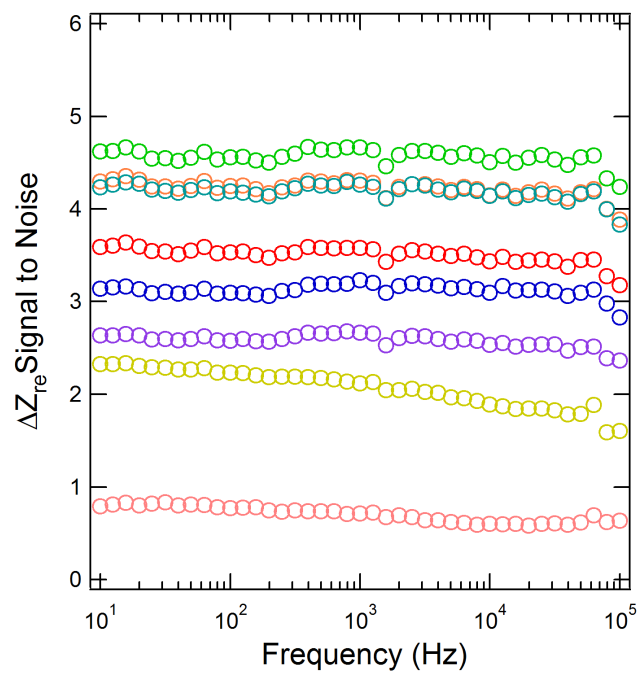
Zn(II)



Fe(III)

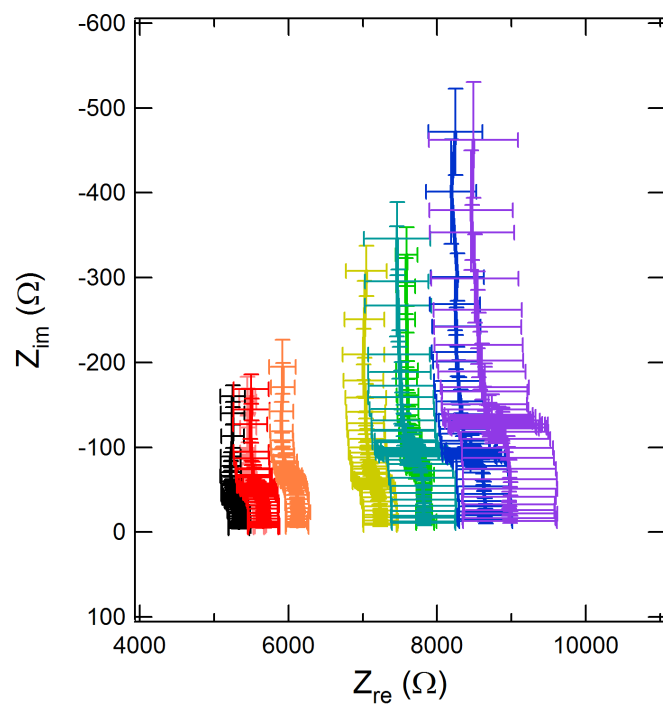


Zn(II)

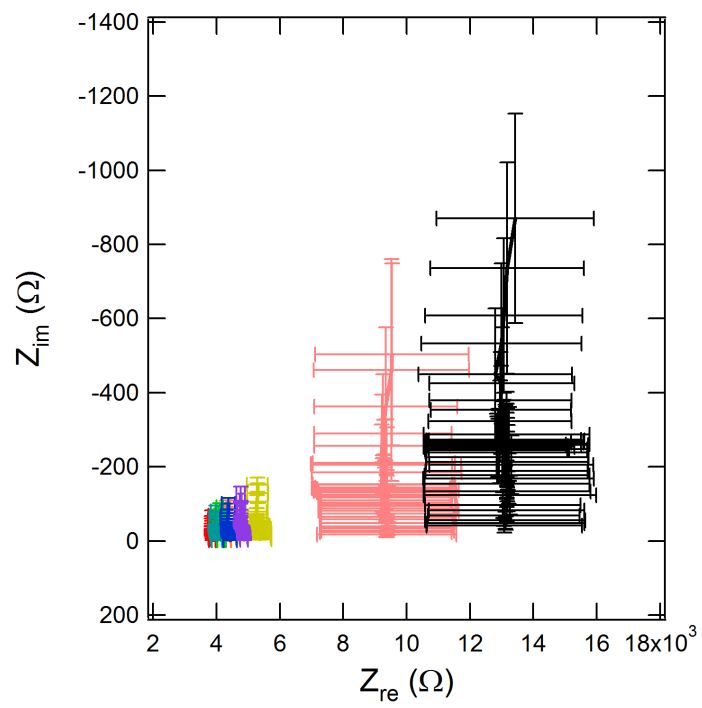


B.2.2 S2

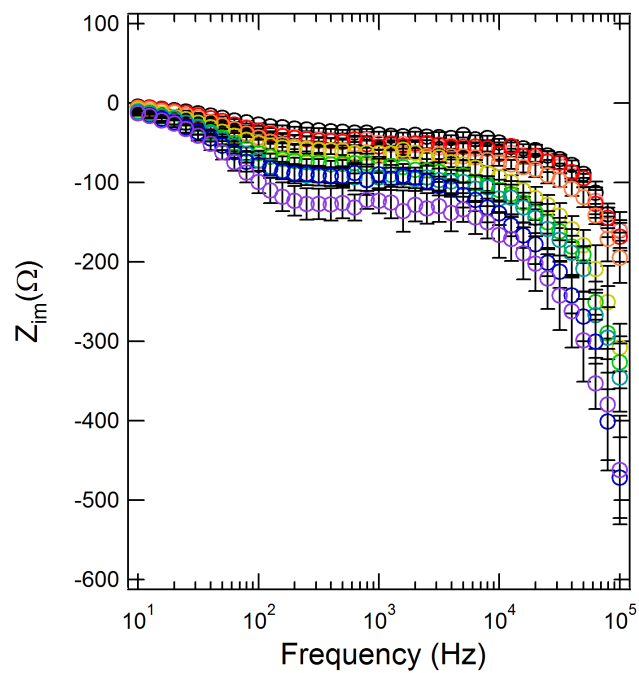
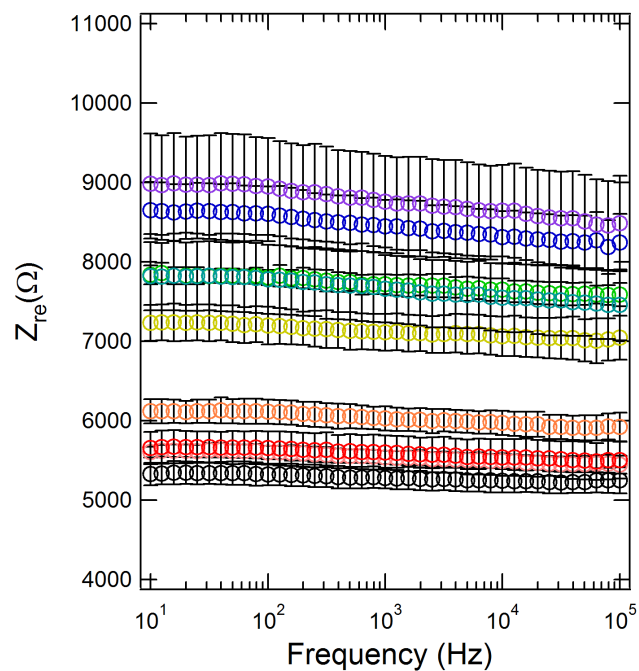
Fe(III)



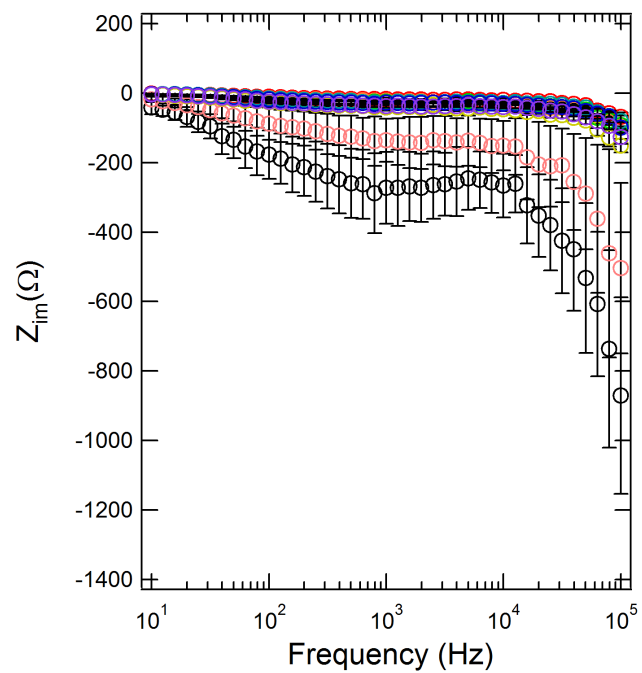
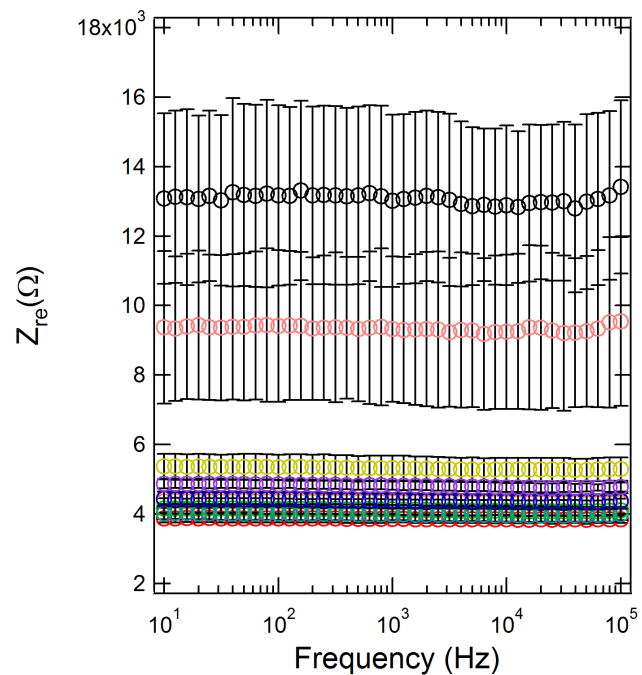
Zn(II)



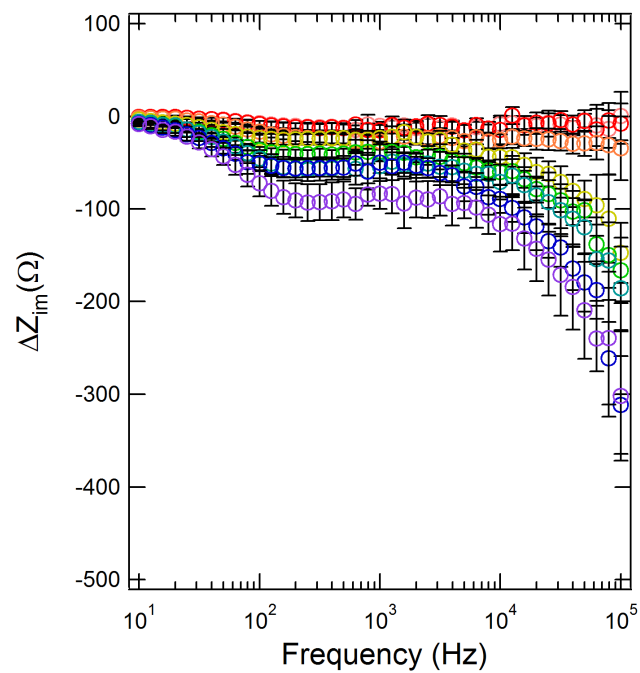
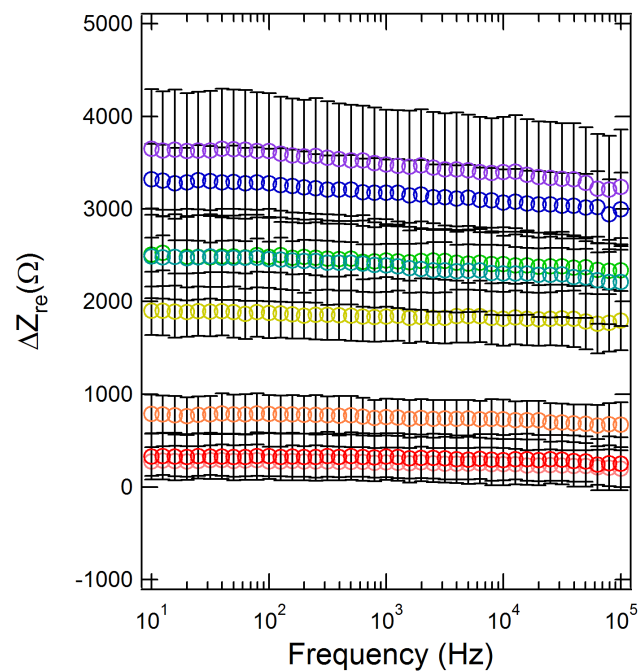
Fe(III)



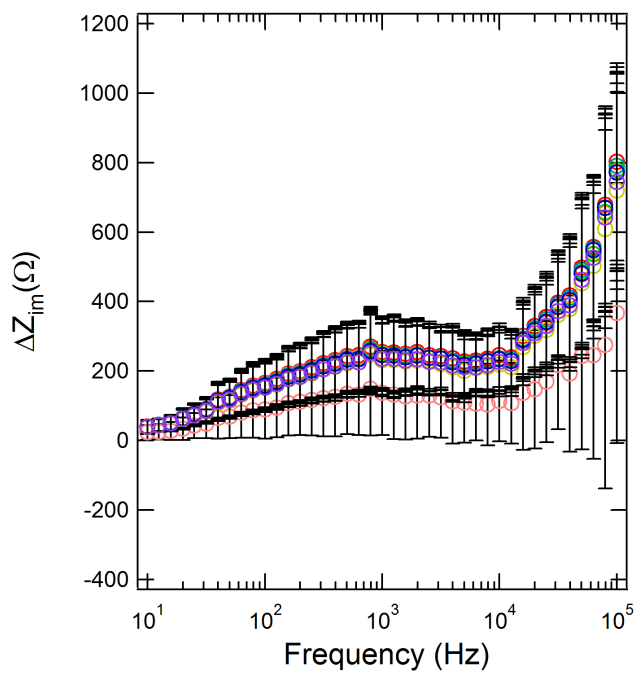
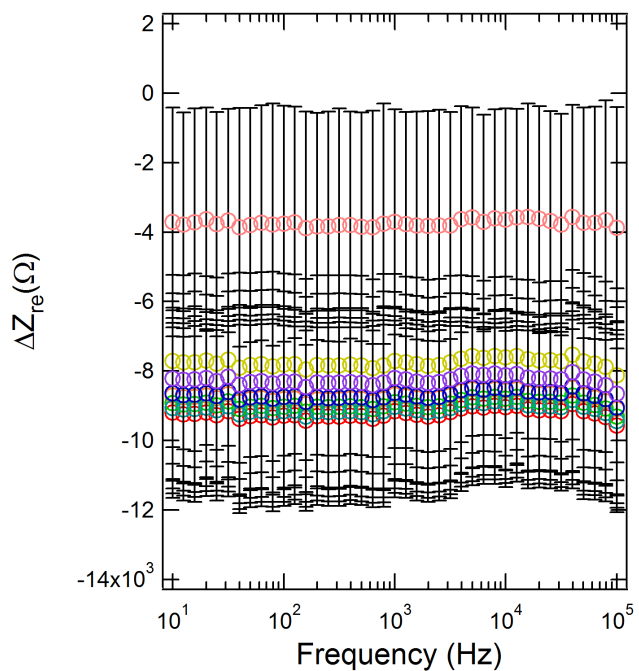
Zn(II)



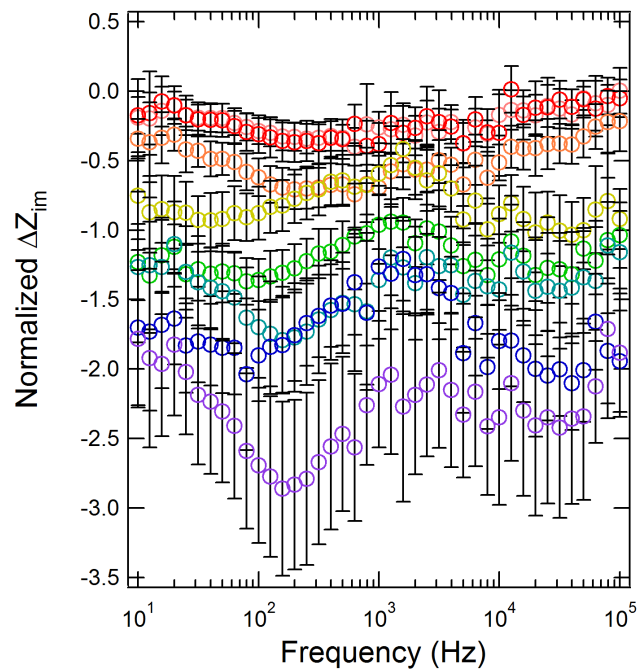
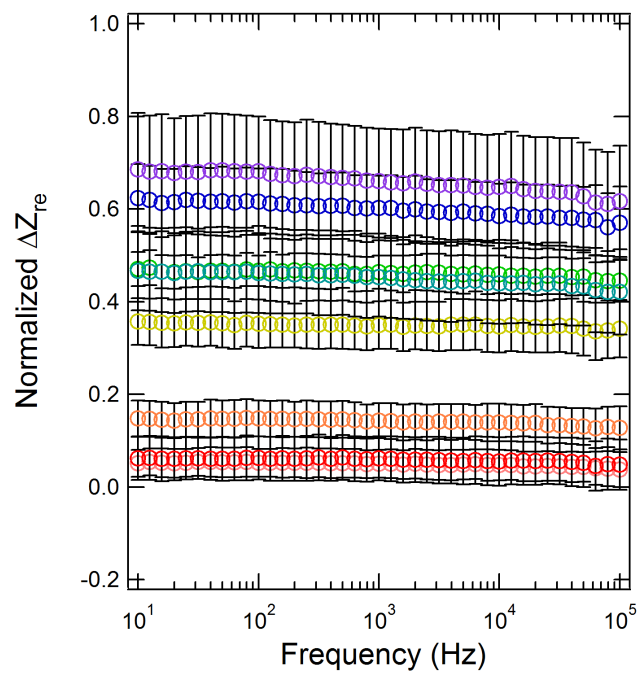
Fe(III)



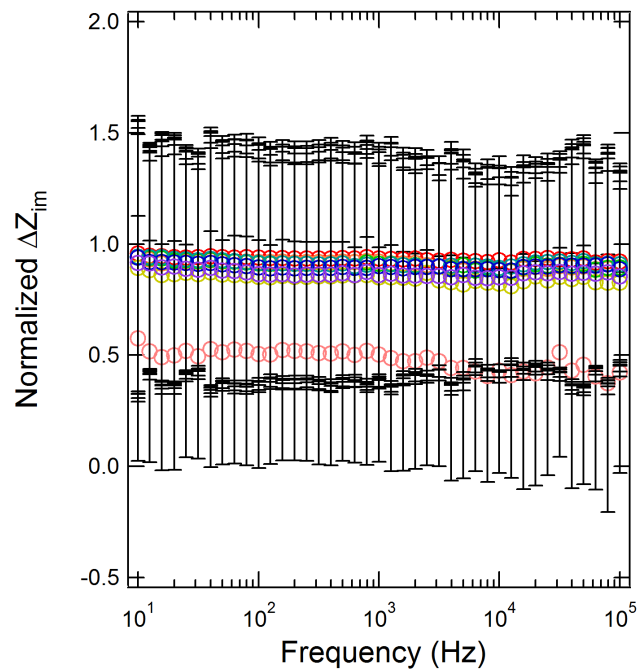
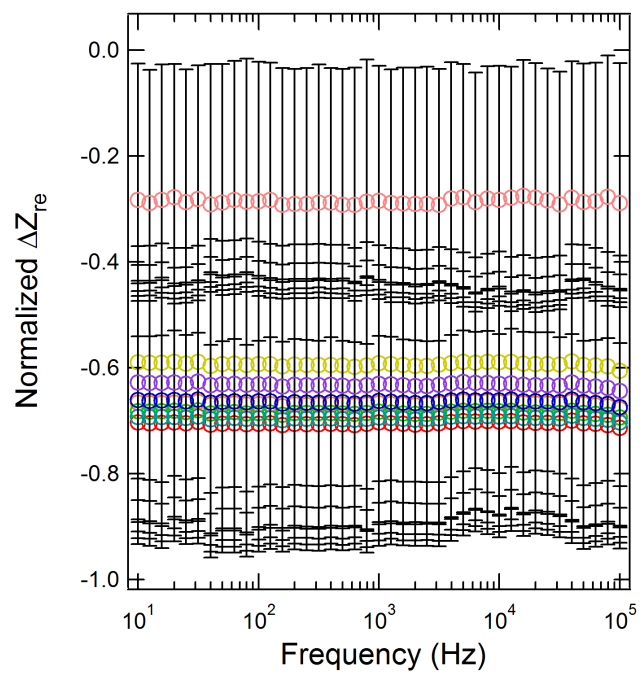
Zn(II)



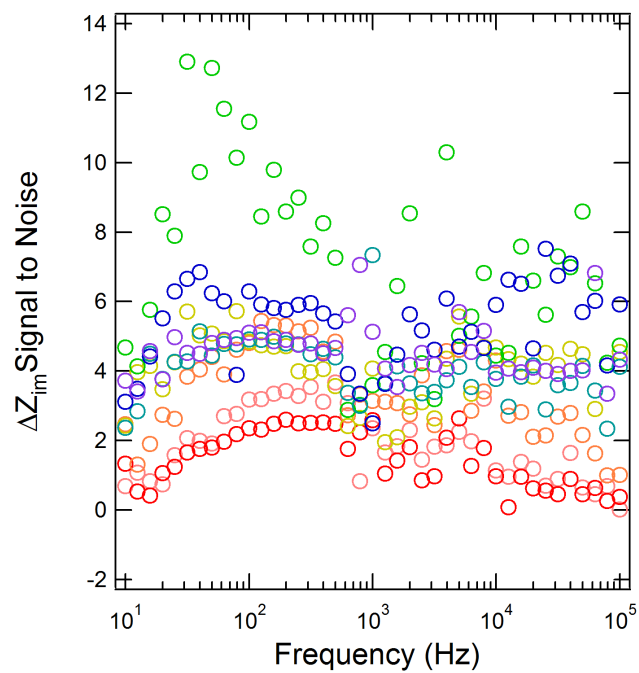
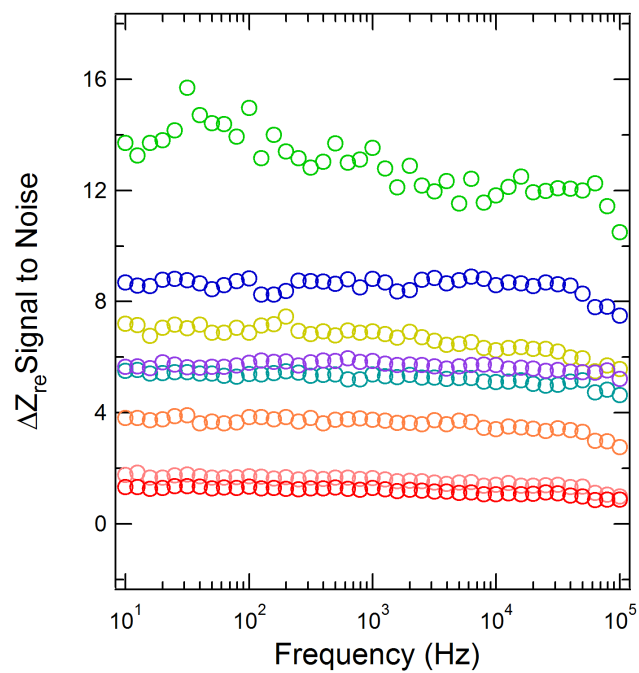
Fe(III)



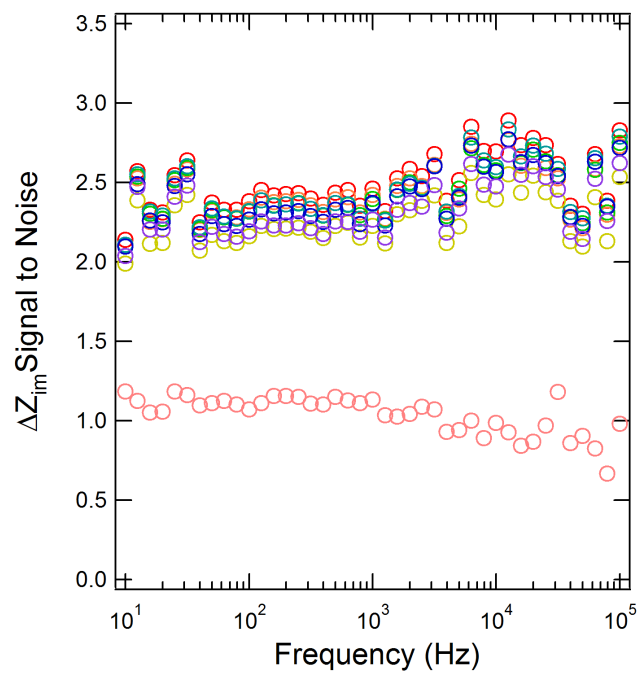
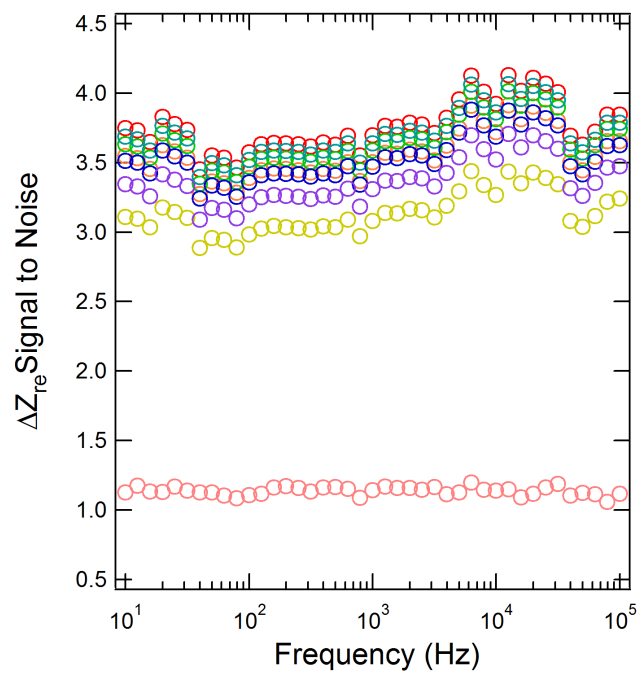
Zn(II)



Fe(III)



Zn(II)



B.2.3 Coefficient of Determination R^2 vs. Frequency

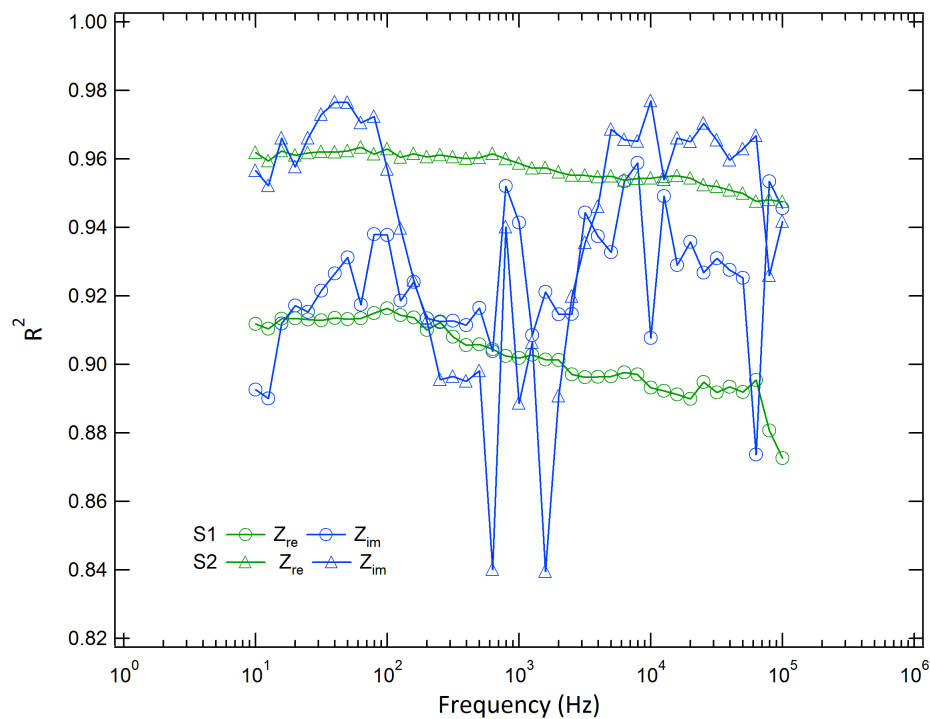


Figure B.1: Coefficient of determination R^2 vs. EIS frequency showing the goodness of fit for a linear relationship between the normalized change in real/imaginary impedance vs. $\log[\text{Fe}^{3+}]$.