PLASMA ELECTROCHEMICAL REDUCTION FOR NANOMATERIALS
SYNTHESIS AND ASSEMBLY

by

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Submitted in partial fulfillment of the requirements
For the degree of Doctor of Philosophy

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(date) 03/16/2012

*We also certify that written approval has been obtained for any proprietary material contained therein.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vi</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ix</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>xii</td>
</tr>
</tbody>
</table>

## CHAPTER

### 1. INTRODUCTION AND MOTIVATION FOR NANOFABRICATION

- 1.1 Nanofabrication: The assembly of nanomaterials                     | 1    |
- 1.2 Plasma-assisted nanomaterial synthesis and nanofabrication         | 4    |
- 1.3 Plasma electrochemistry                                            | 5    |
- 1.4 Nanofabrication via plasma electrochemical reduction               | 8    |

### 2. ELECTRON TRANSFER REACTION AT THE PLASMA-LIQUID INTERFACE

- 2.1 Introduction                                                       | 10   |
- 2.2 Experimental details                                              | 11   |
- 2.3 Results and discussion                                             | 20   |
- 2.4 Summary                                                           | 34   |

### 3. DIRECT WRITING OF PATTERNED METAL NANOPARTICLES

- 3.1 Introduction                                                       | 35   |
- 3.2 Experimental details                                              | 36   |
- 3.3 Results and discussion                                             | 40   |
- 3.4 Summary                                                           | 54   |

### 4. EXTRACTION OF A LOW-CURRENT DISCHARGE AT AMBIENT CONDITIONS

- 4.1 Introduction                                                       | 55   |
- 4.2 Experimental details                                              | 57   |
- 4.3 Results and discussion                                             | 59   |
- 4.4 Summary                                                           | 69   |
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1. Measurements of voltage in plasma-liquid electrochemical cell</td>
<td>13</td>
</tr>
<tr>
<td>Table 2.2. Measurements of discharge current in plasma-liquid electrochemical cell</td>
<td>14</td>
</tr>
<tr>
<td>Table 2.3. Summary of ferricyanide reduction experiments</td>
<td>22</td>
</tr>
<tr>
<td>Table 2.4. pH measurement in plasma-liquid experiments</td>
<td>26</td>
</tr>
<tr>
<td>Table 4.1. XPS analysis of plasma reduced Ag films</td>
<td>65</td>
</tr>
<tr>
<td>Table 6.1. Atomic percentage of different carbon bonds in reduced GO films</td>
<td>103</td>
</tr>
<tr>
<td>Table 6.2. XPS analysis of carbon and oxygen content and sheet resistance of reduced GO films</td>
<td>105</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1</td>
<td>Schematic of plasma</td>
<td>5</td>
</tr>
<tr>
<td>Figure 1.2</td>
<td>Photograph of microplasma</td>
<td>6</td>
</tr>
<tr>
<td>Figure 1.3</td>
<td>Schematic of plasma-liquid electrochemical cell</td>
<td>7</td>
</tr>
<tr>
<td>Figure 1.4</td>
<td>Flow chart of plasma electrochemistry</td>
<td>9</td>
</tr>
<tr>
<td>Figure 2.1</td>
<td>Schematic of electron transfer reaction</td>
<td>11</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Schematic of voltage drop measurement</td>
<td>13</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>UV-vis spectra of K₃Fe(CN)₆ and K₄Fe(CN)₆</td>
<td>15</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>Calibration curve for UV-vis spectra of K₃Fe(CN)₆ and K₄Fe(CN)₆</td>
<td>16</td>
</tr>
<tr>
<td>Figure 2.5</td>
<td>UV-vis spectra of K₃Fe(CN)₆ and K₄Fe(CN)₆ as a function of pH</td>
<td>17</td>
</tr>
<tr>
<td>Figure 2.6</td>
<td>CV for K₃Fe(CN)₆ and K₄Fe(CN)₆ at varying relative concentrations</td>
<td>18</td>
</tr>
<tr>
<td>Figure 2.7</td>
<td>Calibration curve for CV of K₃Fe(CN)₆ and K₄Fe(CN)₆</td>
<td>18</td>
</tr>
<tr>
<td>Figure 2.8</td>
<td>Comparison of the reduced ferricyanide percent (UV-vis vs. CV)</td>
<td>19</td>
</tr>
<tr>
<td>Figure 2.9</td>
<td>UV-vis and CV analysis of plasma reduced Fe(CN)₆⁻³</td>
<td>21</td>
</tr>
<tr>
<td>Figure 2.10</td>
<td>Solution potential measurement as a function of time</td>
<td>24</td>
</tr>
<tr>
<td>Figure 2.11</td>
<td>pH measurement in plasma-liquid experiments</td>
<td>25</td>
</tr>
<tr>
<td>Figure 2.12</td>
<td>TEM images of Ir nanoparticles</td>
<td>28</td>
</tr>
<tr>
<td>Figure 2.13</td>
<td>XPS spectra of Ir nanoparticles</td>
<td>30</td>
</tr>
<tr>
<td>Figure 2.14</td>
<td>XPS spectra of chemically synthesized Ir nanoparticles</td>
<td>31</td>
</tr>
<tr>
<td>Figure 2.15</td>
<td>XPS spectra</td>
<td>32</td>
</tr>
<tr>
<td>Figure 2.16</td>
<td>XPS spectra of plasma reduced Ir nanoparticles (with citric acid)</td>
<td>32</td>
</tr>
<tr>
<td>Figure 2.17</td>
<td>Amperometric response and calibration plot</td>
<td>33</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Schematic of direct writing approach</td>
<td>41</td>
</tr>
</tbody>
</table>
Figure 3.2. UV-vis characterization of direct writing approach .................. 43
Figure 3.3. XRD characterization of direct writing approach ...................... 44
Figure 3.4. SEM characterization of direct writing approach ...................... 45
Figure 3.5. Optimization of direct writing approach ................................ 47
Figure 3.6. TEM characterization of direct writing approach ...................... 48
Figure 3.7. Histograms of particle size distribution ................................ 48
Figure 3.8. A control experiment for plasma electrochemical reduction of films 50
Figure 3.9. Patterned InAs nanowires .................................................. 51
Figure 3.10. Patterned InAs nanowires grown at different conditions .......... 52
Figure 4.1. Schematic of a low-current discharge and lithographical approach.. 59
Figure 4.2. I-V characteristic of extracted discharge .............................. 60
Figure 4.3. Microplasma current as a function of extracted discharge current... 62
Figure 4.4. Photos of extracted discharge ............................................. 63
Figure 4.5. XPS spectra of Ag 3d after exposure to extracted discharge ........ 64
Figure 4.6. SEM images of alumina membrane templates ........................ 66
Figure 4.7. SEM images of patterned AgNO₃/PVA .................................. 67
Figure 4.8. SEM images of AgNO₃/PVA patterned by scanning ................... 67
Figure 4.9. Photos of a pattern transferred directly by extracted discharge ...... 68
Figure 5.1. Schematic of directed assembly ........................................... 76
Figure 5.2. Morphological characterization of metallopolymer .................... 77
Figure 5.3. WAXS characterization before and after annealing ................... 79
Figure 5.4. TEM images of [Pt₂(1)Cl₂](Cl₂) after plasma exposure ............. 80
Figure 5.5. TEM images of [Pt₂(2)Cl₂](Cl₂) after plasma exposure ............. 81
Figure 5.6. TEM images of [Pt_2(3)Cl_2](Cl_2) after plasma exposure .......................... 82
Figure 5.7. XPS characterization before and after reduction................................. 83
Figure 5.8. XPS spectra as function of Ar^+ sputter time.................................. 83
Figure 5.9. TEM images after alternative reduction schemes .............................. 85
Figure 5.10. TEM images after electron beam exposure.................................... 85
Figure 5.11. TEM images of Pt NPs after electron beam exposure...................... 87
Figure 5.12. Comparison of directed assembly for various metallopolymers........ 87
Figure 5.13. Particle size and density characterization........................................ 88
Figure 6.1. Schematic of remote plasma-assisted GO reduction.......................... 98
Figure 6.2. Temperature measurement of remote plasma................................. 100
Figure 6.3. OES spectra of Ar/H_2 microplasma........................................... 101
Figure 6.4. XPS spectra of GO films after thermal and plasma reduction ........... 102
Figure 6.5. XPS survey spectra of GO films after thermal and plasma reduction.. 103
Figure 6.6. Atomic percentage and atomic ratio in reduced GO films............... 104
Figure 6.7. Raman spectra as a function of laser exposure time.......................... 106
Figure 6.8. Raman spectra of reduced GO films ............................................. 107
Figure 6.9. Raman spectra of CVD graphene after remote plasma exposure....... 108
Figure 7.1. Graphene exfoliation based on plasma-liquid electrochemistry ........ 113
Figure 7.2. SEM image of FIB patterned 3C-SiC membrane.............................. 115
Plasma Electrochemical Reduction for Nanomaterials Synthesis and Assembly

Abstract

By

Seung Whan Lee

The recent development of microscale plasmas allows the formation of ions, electrons, and other energetic species near ambient conditions (i.e. room temperature and atmospheric pressure). As a source of charged species, microplasmas are suitable for novel electrochemical applications, for example to initiate electrochemical reactions through the reaction of gas-phase electrons with ionic solutions or ionic films.

In this dissertation, we demonstrate several examples of plasma electrochemistry with the purpose of synthesizing and assembling metal nanoparticles. To better understand and study the role of gas-phase electrons in plasma electrochemistry, we initially study a model reaction in solution, the reduction of ferricyanide to ferrocyanide. Our experiments show that a microplasma can indeed reduce ferricyanide, confirming
that a plasma discharge can serve as a source of electrons for electrochemical reactions in solution.

These studies then lead to the main focus of the dissertation which is reduction of metal ions dispersed on surfaces to fabricate patterns of nanomaterials. Towards this end, we present three general approaches to nanofabrication based on plasma electrochemistry 1) direct writing of metal nanoparticles, 2) lithographic pattern transfer of metallic materials at the nanoscale, and 3) directed assembly of metal nanoparticles via metallopolymer-based molecular templates. Direct writing of metal nanoparticles is achieved by exposing spin-coated films of metal salts and polymer to a rastered microplasma. As the films are exposed to the plasma, the metal ions are reduced and nanoparticles are nucleated. Thus, patterns of size close to the microplasma (~100 μm) are transferred to a film to produce a flexible, patterned film of metal nanoparticles. To reduce the pattern size, we have extracted a low-current discharge from the main microplasma discharge and incorporated a nanomask such as an alumina membrane template to transfer patterns by lithography. The extracted discharge allows electrons to interact with the patterned film without ion bombardment. Further reduction in the resolution of the transferred patterns is achieved by metallo-supramolecular polymer chemistry. These novel materials contain inorganic (metal) moieties and self assemble into films with macroscopic order. Reduction of the metal component by plasma electrons results in the formation of well-dispersed, nanometer-sized (<3 nm) metal nanoparticles with long-range order. Overall, these approaches to nanopatterning based on plasma electrochemistry are low cost and scalable and amenable to roll-to-roll
processing which is attractive for emerging technological applications in catalysis, energy, and medicine.
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Without help from my advisors, my collaborators, and my family, my achievements would not have been possible.

My advisor, Dr. Mohan Sankaran, is more than an advisor to me. As my advisor, Dr. Sankaran helped me develop my research; as my mentor, he helped me develop my teaching philosophy. During Ph.D. program, Dr. Sankaran gave me a lot of opportunities to mentor undergraduate student and high school student. Initially, it required too much patience. However, I immediately realized that Dr. Sankaran wanted to give me the opportunity to develop an educational philosophy. I believe that all of the moment with him will be guide lines for my future.

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(Electrical Engineering at CWRU) designed extracted discharge system. The collaboration with Dr. Manish Chhowalla and Dr. Cecilla Mattevi (Material Science and Engineering at Rutgers University) developed low temperature graphene oxide reduction system.

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Cleveland, Ohio

March 2012
1.1 Nanofabrication: The assembly of nanomaterials

The term “nanotechnology” is now around us everywhere and used to describe the creation and exploitation of materials with structural features at length scales of approximately 1-100 nanometers (nm). Nanoscale materials or nanomaterials are materials that exhibit properties different than their bulk counterparts [1]. The enormous interest in nanomaterials is driven by the possibility of assembling materials with tunable properties, also referred to as nanofabrication. Nanofabrication can lead to new science as well as new products, devices, and technologies. Examples of nanomaterials include nanoparticles (metal or semiconducting), carbon nanotubes, semiconductor nanowires, and graphene. The past decade has witnessed tremendous growth in the field of nanomaterials, in part due to pressure from the electric industry to keep pace with Moore’s Law [2] which forecasts the doubling of device density on integrated circuits every 18 months. However, the assembly of nanomaterials, i.e. nanofabrication, remains a challenge.

Perhaps the most well-studied nanomaterial is metal nanoparticles [3, 4]. Nanofabrication of metal nanoparticles to obtain well-defined arrays is important for several technologies including sensors [5, 6], magnetic data storage [7], flash memory [8], and catalysis [9], to name a few. Currently, there are three general strategies for generating patterns of metal nanoparticles: (i) lithographic methods, (ii) direct writing,
and (iii) self- or directed assembly. Each of these approaches has its own advantages and disadvantages which we summarize below.

**i. Lithographic methods:** The most straightforward and “brute force” approach for generating patterns of nanoparticles is lithography. In this technique, polymer masks or templates are used to transfer a desired pattern to a substrate. The resolution of the transferred pattern is determined by the type of lithography. There are currently several approaches to lithography including photolithography [10], microcontact printing [11,12], nanoimprint lithography [13], and stencil lithography [14]. In general, although lithography is good for fabricating a prototype, the multiple processing steps make it too expensive and time consuming for large-scale applications. Moreover, the resolution of the transferred patterns remains approximately 10 nm.

**ii. Direct writing:** The development of scalable methods that effectively pattern nanoparticles with high resolution is a key step towards the commercial exploitation of these novel materials [15]. In this context, direct writing is a powerful tool that enables the deposition of metal nanoparticles in any arbitrary pattern. Solution-based direct writing approaches include inkjet printing [16,17], dip-pen nanolithography (DPN) [18], laser printing [19] and electrostatic-driven deposition [20]. A potential drawback of these techniques is that chemical steps are required to prepare the nanoparticle inks and the metal nanoparticles must have an affinity for the substrate that is used. Alternatively, dry direct-writing approaches based on electron beams [21,22], X-rays [23,24], or lasers [25,26] can deposit patterns from metal precursors with excellent resolution (< 10 nm). Unfortunately, these techniques remain too expensive and low-throughput for large-scale manufacturing.
iii. Self- or directed-assembly: A potentially interesting alternative to lithography and direct writing is the assembly of nanomaterials by either self assembly, which occurs through physical and chemical interactions between the materials and the substrate, or directed assembly, whereby a molecular template is used to aid the assembly of the materials. Both self- and directed-assembly are low cost and large scale. An example of directed assembly is the implementation of block copolymers in metal nanoparticle deposition [27, 28, 29]. Although patterned metal nanoparticles based on block copolymer templates are easily formed over a large area with high fidelity, a challenge that remains is a priori knowledge of how the block copolymers assemble and how different metals can be deposited. In addition, the resolution of block copolymers remains around 10 nm [30].

While significant progress has been made through lithographic, direct writing, and self/directed assembly approaches, nanofabrication has not reached the stage of commercialization. Further improvements are required in each of these approaches to lower cost, improve resolution, and make them generic so that a wide range of materials can be processed. The goal of this dissertation is to develop new chemical approaches for nanofabrication that address these various issues and create avenues for nanofabrication to be implemented in an industrial environment.
1.2 Plasma-assisted nanomaterial synthesis and nanofabrication

Over the last two decades, plasma processing has played a critical role in the manufacturing of materials for many industries such as the electronic industry where plasmas are used to fabricate integrated circuits. The unique properties of plasma-based processes such as low temperature and high-purity are essential to high-fidelity pattern transfer. However, these processes are normally operated at low pressure which can entail large costs associated with operation and maintenance of vacuum equipment. Alternatively, operation near or at atmospheric pressure would be potentially cheaper, easier to implement, and highly desirable for industrial applications [31]. Therefore, one of the important challenges in plasma processing is the development of low-temperature (i.e. cold), atmospheric-pressure plasma sources. The availability of this class of plasmas is expected to open new applications in medicine [32, 33, 34], gas treatment [35, 36], textiles [37], surface modification [38, 39], and nanofabrication [40, 41]. Here, we are interested in developing atmospheric-pressure plasmas for nanofabrication applications. The possibility of creating patterned architectures of nanomaterials at atmospheric pressure and low cost has the potential to revolutionize materials manufacturing.
1.3 Plasma electrochemistry

A new fundamental idea that has been developed as part of this dissertation is plasma electrochemistry. Conventional electrochemical reactions are generally driven in a solution at the interface of an electron conductor (a metal or a semiconductor) and an ionic conductor (the electrolyte), which involves electron transfer between the electrode and the electrolyte or species in solution. Plasmas are potentially suitable for electrochemical applications since ionized species are present which can similarly drive charge transfer reactions [Figure 1.1]. However, unlike electrochemical reactions in liquid (or solid), the charge exchange occurs between the gas and liquid (or solid).

Although plasmas have found numerous chemical and materials applications, only a few previous reports of electrochemical applications exist. Over 100 years ago, Gubkin studied plasma discharges at the surface of an aqueous solution of silver nitrate and observed the formation of metallic silver film [42]. Later, Hickling introduced the idea of glow discharge electrolysis (GDE) whereby electrochemical reactions such as water electrolysis were initiated by a plasma electrode [43, 44]. Despite these early studies that motivated the use of plasmas in electrochemistry, plasmas have not been widely

![Diagram of plasma containing electron, positive ions, and neutral (excited and ground state) species.](image-url)

Figure 1.1. Plasmas contain electron, positive ions, and neutral (excited and ground state) species.
implemented in electrochemical applications mostly because stable operation remains elusive.

Recently, there has been renewed interest in plasma-liquid systems for the synthesis of metal nanoparticles [45, 46, 47, 48, 49, 50, 51, 52, 53]. We note that only a some of these experiments fall under the category of plasma electrochemistry because of their electrode configuration. Figure 1.3 shows a side-by-side comparison of a standard electrochemical cell vs. a plasma-liquid electrochemical cell. In a standard electrochemical cell, metal cations created from anodic dissolution of metal foils or present in the electrolyte are reduced at the cathode to nucleate metal particles at the electrolyte/electrode interface [54]. Isolation of the reduction products is difficult because of the presence of the solid electrode [55, 56, 57]. Replacing the solid electrode with a plasma allows a gaseous electrode to initiate electrochemical reactions. In

Figure 1.2. Photo of a DC microplasma jet formed at atmospheric pressure in a flow of argon between a metal capillary tube and a grounded metal mesh.
comparison to the standard electrochemical cell, the plasma electrochemical cell facilitates the synthesis of metal nanoparticles.

The earliest report of plasma-liquid electrochemical reduction was the reduction of a platinum salt ($\text{H}_2\text{PtCl}_6$) by a $\text{H}_2$ plasma [47]. In this case, atomic hydrogen generated in the plasma was found necessary to reduce the Pt cations to metallic Pt nanoparticles. More recently, Ar or $\text{O}_2$ plasmas have been used to reduce metal cations in solution (no $\text{H}_2$) [58]. In these cases, the mechanism for plasma reduction remains unclear. Plasmas formed with water could generate oxidizing or reducing agents in solution by electron impact dissociation or UV irradiation including hydrogen and hydroxyl radicals, hydrogen gas, and hydrogen peroxide which may be responsible for reduction. In this thesis, we will address the role of electrons in plasma-electrochemical reduction.

![Figure 1.3](image)

**Figure 1.3.** (a) Conventional electrochemical cell, (b) Plasma – liquid electrochemical cell.
1.4 Nanofabrication via plasma electrochemical reduction

Although plasma electrochemical reduction has been successfully developed to reduce metal cations and form metal nanoparticles in solution, for various applications, it is important to assemble the nanoparticles, as discussed in Section 1.1. Towards this end, the combination of plasma electrochemical reduction to synthesize metal nanoparticles and patterning approaches (e.g. lithography, direct writing, self/directed assembly) is of interest to create a new chemical approach to nanofabrication that is potentially low cost and scalable.

In this dissertation, we are focused on the development of new nanofabrication techniques based on plasma electrochemistry [Figure 1.4]. To first provide insight into the basic fundamentals of plasma electrochemistry, in Chapter 2, we present studies of a model electrochemical reaction, the reduction of ferricyanide to ferrocynaide. We then pursued an application of plasma-liquid electrochemistry, the synthesis of metal nanoparticles for biosensor applications. The remainder of the thesis is focused on nanofabrication, i.e. the assembly of nanomaterials as thin films, by plasma electrochemistry. We have pursued three strategies for nanofabrication via plasma electrochemistry: (i) direct writing [Chapter 3], (ii) lithography [Chapter 4], (iii) directed assembly [Chapter 5]. Whereas the bulk of the thesis is focused on inert plasmas (i.e. Ar gas), we have to a small extent explored reactive plasmas with H₂ gas; these studies as they apply to the reduction of graphene oxide are presented in Chapter 6. These studies could be eventually combined with our patterning techniques to enable nanofabrication of novel graphene materials.
Figure 1.4. Flow chart for dissertation encompassing our work on plasma electrochemical reduction.
CHAPTER 2
ELECTRON TRANSFER REACTION AT THE PLASMA-LIQUID INTERFACE

2.1 Introduction

Plasma electrochemistry encompasses the idea that charge states in a plasma discharge such as electrons can initiate electrochemical reactions in solution or at surfaces through charge transfer. While several studies of plasmas in contact with liquids have been reported in the literature, it remains unclear how gas-phase electrons interact with ions in solutions in comparison to electrochemical systems involving metal electrodes. In this chapter, we report for the first time evidence of electron-transfer reactions at the plasma–liquid interface. Our study is enabled by the recent development of a nonthermal, atmospheric-pressure microplasma source [59] which can be stably formed on a solution surface at ambient conditions. Using the ferricyanide/ferrocyanide redox couple as a model system, we show that charge transfer depends on the properties of the discharge; for example, the reduction rate of ferricyanide is found to increase with discharge current, which in turn is related to the flux of plasma electrons to the solution surface. These findings open a new direction for electrochemistry where gas-phase electrons with tunable fluxes or energies are used to initiate and control electrochemical reactions in solution. We demonstrate that this chemical approach facilitates the synthesis of metal nanoparticles in solution such as iridium which can be used in biosensor applications. In addition, our experiments in liquid serve as background for our work with films where metal ions dispersed in a polymer are reduced to form patterns of metal nanoparticles. These results will be discussed in subsequent chapters.
2.2 Experimental details

Experimental setup: Plasma electrochemical reactions in solution were carried out with a glass cell (Adams & Chittenden) schematically depicted in Figure 2.1a. The electrolytes in the anodic and cathodic sides were prevented from mixing by a fritted glass plug. Separate compartments for the cathode and anode permitted isolation of the half-cell reaction occurring at the plasma–liquid interface. An Ag/AgCl mesh (12.5 × 12.5 mm Ag mesh, 0.115 mm dia. wire, Alfa Aesar) chlorided in 3 M KCl at 1 mA/cm² was immersed in the anolyte to serve as the anode – this also served as a reference electrode for potential measurements. A stainless steel capillary tube (180 μm i.d. × 5 cm length, Varian, Inc.) was positioned 2 mm away from and normal to the surface of the catholyte.

![Schematic and photograph of electrochemical cell with a gaseous cathode electrode.](image)

Figure 2.1. Schematic (a) and photograph (b) of electrochemical cell with a gaseous cathode electrode. An atmospheric-pressure microplasma was formed in an Ar gas flow between a stainless-steel capillary tube and the electrolyte surface. The anode electrode was Ag/AgCl.
using a micrometer-controlled linear stage and fed with argon gas flow. A microplasma was ignited in the exit argon flow and sustained by a negatively biased DC power supply [Figure 2.1b]. During experiments, the microplasma impinged on the surface of the catholyte, over a surface area of ~1 mm², to serve as the gaseous cathode. Over the course of an experiment, the temperature of the bath increased by no more than 5 °C. No stirring was applied in order to avoid disturbing the solution surface and minimize fluctuations in the discharge current.

We chose a model reaction, the reduction of ferricyanide [Fe(CN)₆³⁻] to ferrocyanide [Fe(CN)₆⁴⁻], to study interactions of plasma electrons with the ionic electrolyte. The catholyte and anolyte solutions consisted of 0.2 mM potassium ferricyanide [K₃Fe(CN)₆] and 0.1 M KCl in deionized water, and 0.1 M KCl in deionized water, respectively. Experiments were initiated by igniting the plasma which resulted in current flow through the cell, and allowed to run for 2 to 15 min. The metal capillary tube was cleaned between trials by pushing a tungsten wire through the capillary tube, polishing the outside surface with sand paper, and sonicating in acetone.

Voltage and current measurements: Initially, we measured the voltage drops across resistors in our electrical circuit [see Figure 2.2] to obtain and compare the discharge currents on the cathode and anode sides (discharge current and cell current are synonymous in our case). A large ballast resistor on the cathode side, R_{cathode}=325.2 kΩ, was used to control the discharge current. A smaller resistor on the ground side, R_{anode}=500 Ω, was used to measure the discharge current on the anode side. Voltages greater than 1000 V were measured with a high voltage probe (Oscilloprobe P4100,
Figure 2.2 Schematic of electrical circuit and voltage drops measured to obtain discharge current (i.e. cell current) at the anode and cathode sides.

Table 2.1 Voltage drops measured at various points in our electrical circuit shown in Figure 2.2. The power supply voltage is distributed through a ballast resistor ($R_{\text{cathode}}$), the gas discharge, the cell, and a current measuring resistor ($R_{\text{anode}}$) [we note that the power supply was a negative high voltage source]. $V_{\text{cathode}}$ refers to the voltage drop across the ballast resistor (325.2 kΩ), $V_{\text{cathode-anode}}$ refers to the voltage drop between the cathode electrode (i.e. metal capillary tube) and the anode electrode (i.e. Ag/AgCl), and $V_{\text{anode}}$ refers to the voltage drop across the current measuring resistor (500 Ω) resistor. As the power supply voltage is increased, the voltage drops increase and the discharge (or cell) current increases.

<table>
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<tr>
<td>-1799</td>
<td>-1600</td>
<td>-197</td>
<td>-2.50</td>
</tr>
<tr>
<td>-1959</td>
<td>-1762</td>
<td>-194</td>
<td>-2.75</td>
</tr>
<tr>
<td>-2238</td>
<td>-1920</td>
<td>-315</td>
<td>-3.00</td>
</tr>
</tbody>
</table>
100:1 V). Table 2.1 shows typical values of the voltage drops across the resistors and the corresponding currents – we note that the voltage from the power supply is distributed across $R_{\text{cathode}}$, the gas discharge, the cell, and $R_{\text{anode}}$. The voltage drop across the gas discharge and the cell are combined and shown as $V_{\text{cathode-anode}}$. Our measurements show that as the power supply voltage is raised, the voltage drops increase and, therefore, the current through the cell (or discharge) is increased. The currents, obtained from the voltage drops across $R_{\text{cathode}}$ or $R_{\text{anode}}$, (specified as $i_{\text{cathode}}$ and $i_{\text{anode}}$) were found to differ by less than 2% [Table 2.2], confirming that there were negligible current losses through the electrochemical cell.

*Calibration curves for ultraviolet-visible (UV-vis) absorbance measurements:* The ferricyanide concentration in solution as a function of time after plasma exposure was

<table>
<thead>
<tr>
<th>$i_{\text{cathode}}$ (mA)</th>
<th>$i_{\text{anode}}$ (mA)</th>
<th>Current difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.96</td>
<td>2.00</td>
<td>2.2</td>
</tr>
<tr>
<td>2.45</td>
<td>2.50</td>
<td>1.9</td>
</tr>
<tr>
<td>2.95</td>
<td>3.00</td>
<td>1.8</td>
</tr>
<tr>
<td>3.44</td>
<td>3.50</td>
<td>1.8</td>
</tr>
<tr>
<td>3.93</td>
<td>4.00</td>
<td>1.7</td>
</tr>
<tr>
<td>4.43</td>
<td>4.50</td>
<td>1.6</td>
</tr>
<tr>
<td>4.92</td>
<td>5.00</td>
<td>1.5</td>
</tr>
<tr>
<td>5.42</td>
<td>5.50</td>
<td>1.5</td>
</tr>
<tr>
<td>5.91</td>
<td>6.00</td>
<td>1.5</td>
</tr>
</tbody>
</table>
monitored by UV-vis absorbance spectroscopy (Shimadzu UV-1800). Solutions of ferricyanide have a well known absorbance spectrum while ferrocyanide does not absorb [see Figure 2.3]. A calibration curve was obtained by preparing solutions of potassium ferricyanide \([\text{K}_3\text{Fe(CN)}_6]\) and potassium ferrocyanide \([\text{K}_4\text{Fe(CN)}_6]\) with varying relative concentrations (total concentration = 0.2 mM) in 0.1 M KCl (in deionized water) and relating the absorbance intensity at 420 nm. As expected from Beer’s law \((A=\varepsilon Cl)\), the relationship between absorbance intensity and ferricyanide concentration is linear [See Figure 2.4]. Using this calibration curve for ferricyanide absorbance, we obtained the amount of ferricyanide reduced by the plasma at different discharge currents and times by performing UV-vis absorbance spectroscopy on the catholyte solutions after plasma exposure and relating the absorbance intensity to the relative amount of ferricyanide by the following equation:

\[
\% \text{ ferricyanide} = 518 \times (UV \text{ Absorbance at } 420 \text{ nm}) - 1.96
\]

To find the \% ferricyanide reduced, the above equation was simply subtracted from 100:

![Figure 2.3. Absorbance spectra of solutions of K₃Fe(CN)₆ and K₄Fe(CN)₆ at varying relative concentrations (total concentration=0.2 mM) with 0.1 M KCl in deionized water.](image)
The number of molecules that were reduced was then calculated by multiplying the above % ferricyanide reduced in solution by the catholyte volume (15 mL), initial ferricyanide concentration (0.2 mM), and Avogadro’s number. As given by the following reaction,

\[ K_3Fe(CN)_6 + e^- \rightarrow K_4Fe(CN)_6 \]

the number of molecules of ferricyanide reduced is equal to the number of electrons transferred from the plasma to ferricyanide. During plasma exposure, the pH of the solutions increased (as discussed in a following section). To ensure that the pH change did not influence the absorbance of ferricyanide/ferrocyanide, we also collected absorbance spectra and obtained a calibration curve for the absorbance of ferricyanide at different concentrations and pHs. The pH was controlled by adding concentrated NaOH to our solutions. As shown in Figure 2.5, the absorbance intensity of ferricyanide did not
vary with pH over the range that was studied here and the calibration curve at pH=7 was valid.

*Calibration curves for cyclic voltammetry (CV):* To further assess the reduction of ferricyanide, an independent analysis by CV was performed. CV scans were obtained at 2000 rpm from -0.5 V to 0.6 V with a CH Instruments potentiostat and workstation software and a Pine Instruments MSRX motor-speed controller. The three electrode system consisted of a Pt mesh counter electrode, an Ag/AgCl reference electrode, and a glassy carbon rotating disc working electrode from Pine Research Instruments. For each sample, we ran four cycles and averaged the last two scans – representative scans are shown in Figure 2.6. Solutions of potassium ferriycanide \([K_3Fe(CN)_6]\) and potassium ferrocyanide \([K_4Fe(CN)_6]\) in 0.1 M KCl with varying relative concentration (total concentration=0.2 mM) were prepared. A calibration curve was obtained by correlating
Figure 2.6. Cyclic voltammogram (CV) scans of solutions of $\text{K}_3\text{Fe}($CN$)_6$ and $\text{K}_4\text{Fe}($CN$)_6$ at varying relative concentrations (total concentration=$0.2$ mM) with $0.1$ M KCl in deionized water.

Figure 2.7. Calibration curve for cyclic voltammetry (CV) measurements comparing % ferricyanide in solution to current at $0.6$ V. The solutions contained $\text{K}_3\text{Fe}($CN$)_6$ and $\text{K}_4\text{Fe}($CN$)_6$ at varying relative concentrations (total concentration = $0.2$ mM) with $0.1$ M KCl in deionized water.
the currents at 0.6 V in the CV scans to the relative amount (i.e. percent) of ferricyanide in the solutions [Figure 2.7]. The following linear equation was fit to the calibration curve and used to estimate the amount of ferricyanide reduced by the plasma:

\[
\% \text{ ferricyanide} = -5.0 \times 10^6 \times (\text{current at 0.6}) + 104.9
\]

To find the \% ferricyanide reduced, the above equation was simply subtracted from 100:

\[
\% \text{ ferricyanide reduced} = 5.0 \times 10^6 \times (\text{current at 0.6}) - 4.9
\]

We compared the values for \% ferricyanide reduction obtained from our analysis of the CV data with the absorbance results and found excellent correspondence [See Figure 2.8]. However, the absorbance results were considered to be more quantitative since CV measurements can be affected by diffusion and other transport limitations.

**Figure 2.8.** Comparison of percent ferricyanide reduced, as estimated from UV-vis absorbance spectrometry and cyclic voltammetry, at different discharge currents and times.
2.3 Results and discussion

Representative UV-vis absorbance spectra of solutions exposed to a plasma \(i_d = 6\) mA for 0, 5 and, 15 min are shown in Figure 2.9a. The intensity of the absorbance peak at \(\sim 420\) nm is directly proportional to the concentration of \(\text{Fe(CN)}_6^{3-}\) in solution [60], and the decrease over time suggests that \(\text{Fe(CN)}_6^{3-}\) is reduced to \(\text{Fe(CN)}_6^{4-}\) by the plasma [see Figure 2.9a].

Through our calibration procedure, we obtained the percentage of \(\text{Fe(CN)}_6^{3-}\) species reduced by the plasma [Figure 2.9b]. The results show that \(\text{Fe(CN)}_6^{3-}\) is progressively reduced over time, and the rate of reduction is proportional to the discharge current. For a given discharge current, the electron flux (number of electrons per unit area per unit time) delivered to the surface of the solution by the plasma remains constant; thus, the \(\text{Fe(CN)}_6^{3-}\) contained in the solution is reduced at a relatively constant rate. When the discharge current is raised, the electron density in the plasma increases [61], a higher flux of electrons reaches the solution surface, and the rate of reduction increases.

To verify that \(\text{Fe(CN)}_6^{3-}\) was indeed reduced to \(\text{Fe(CN)}_6^{4-}\) and not destroyed by the plasma, we performed cyclic voltammetry. Representative CV of solutions of ferricyanide exposed to a plasma \((i_d = 6\) mA) for 0, 5, and 15 min are shown in Figure 2.9c. A steady-state cathodic current plateau proportional to the \(\text{Fe(CN)}_6^{3-}\) concentration is observed for the initial solution. After plasma exposure, this current plateau decreases and a new anodic current plateau appears, indicating the presence of \(\text{Fe(CN)}_6^{4-}\) in solution and clearly showing that \(\text{Fe(CN)}_6^{3-}\) was reduced to \(\text{Fe(CN)}_6^{4-}\) by the plasma. The current plateaus for \(\text{Fe(CN)}_6^{3-}\) reduction and \(\text{Fe(CN)}_6^{4-}\) oxidation
Figure 2.9. UV-vis absorbance spectra of solutions of Fe(CN)$_6^{3-}$ after 0, 5, and 15 min exposure to a plasma (A), amount of Fe(CN)$_6^{3-}$ reduced as a function of time at discharge currents ($i_d$) of 3 and 6 mA (B), and cyclic voltammograms of solutions of Fe(CN)$_6^{3-}$ after 0, 5, and 15 min exposure to a plasma.
decrease and increase, respectively, by the same magnitude, which confirms that \( \text{Fe(CN)}_6^{3-} \) was not destroyed. The current plateau for \( \text{Fe(CN)}_6^{4-} \) oxidation increases with time as more and more \( \text{Fe(CN)}_6^{4-} \) is generated in solution, consistent with UV–vis absorbance results. For samples analyzed by both spectrophotometric and cyclic voltammetric methods, the estimated amounts of \( \text{Fe(CN)}_6^{3-} \) reduced by the plasma correspond well.

Table 2.3 summarizes our experimental results for reduction of \( \text{Fe(CN)}_6^{3-} \) by the plasma at different discharge currents and times of exposure. The no. of \( \text{Fe(CN)}_6^{3-} \) molecules reduced is obtained from absorbance measurements and the no. of electrons injected is calculated from the cell (i.e. discharge) current.

Table 2.3. Summary of results showing reduction of ferricyanide by the plasma at different currents and times of exposure. The no. of \( \text{Fe(CN)}_6^{3-} \) molecules reduced is obtained from absorbance measurements and the no. of electrons injected is calculated from the cell (i.e. discharge) current.

<table>
<thead>
<tr>
<th>Current (mA)</th>
<th>Exposure Time (min)</th>
<th>Absorbance intensity @ 420 nm</th>
<th>Percent reduction of ( \text{Fe(CN)}_6^{3-} )</th>
<th>No. ( \text{Fe(CN)}_6^{3-} ) molecules reduced</th>
<th>No. electrons injected</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2</td>
<td>0.197</td>
<td>3.80</td>
<td>6.87E+16</td>
<td>2.25E+18</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0.172</td>
<td>16.24</td>
<td>2.93E+17</td>
<td>5.62E+18</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0.165</td>
<td>19.67</td>
<td>3.55E+17</td>
<td>1.12E+19</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>0.133</td>
<td>36.29</td>
<td>6.55E+17</td>
<td>1.68E+19</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>0.188</td>
<td>7.99</td>
<td>1.44E+17</td>
<td>4.49E+18</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>0.170</td>
<td>17.38</td>
<td>3.14E+17</td>
<td>1.12E+19</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>0.104</td>
<td>50.63</td>
<td>9.14E+17</td>
<td>2.25E+19</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>0.076</td>
<td>65.23</td>
<td>1.18E+18</td>
<td>3.37E+19</td>
</tr>
</tbody>
</table>


\[
 n_e = \frac{j}{\mu E e} \tag{1}
\]
where $n_e$ is the electron density, $j$ is the discharge current density (current per unit area), $E$ is the electric field, and $\mu$ is the electron mobility. Despite the evidence for electron transfer, our calculations for the number of electrons injected by the plasma using Faraday’s law indicate that a large number of electrons are not involved in ferricyanide reduction. However, as previously shown, there are no current losses in the cell.

To further address the transfer of electrons from the plasma to the liquid, we measured the solution potential, with respect to an Ag/AgCl reference electrode (Accumet standard high temperature Ag/AgCl reference electrode, Fisher Scientific), by placing a Pt wire in contact with the solution at the plasma–liquid interface. We note that the voltage applied at the plasma electrode by our external power supply is not the conventional electrode potential, since there is a large voltage drop across the plasma. The potential that actually controls the ferricyanide reduction is the solution potential, induced by the plasma at the surface of the catholyte bath. Before igniting the plasma, we measured a surface potential of ~0.43 V, as predicted by the Nernst equation for a nearly pure solution of ferricyanide. We independently calculated the solution potentials by using the Nernst equation which relates the electrochemical potential for a redox couple at different activities (or concentrations for dilute solutions):

$$E_{\text{red}} = E_{\text{red}}^0 - \frac{RT}{zF} \ln \left( \frac{a_{\text{red}}}{a_{\text{ox}}} \right)$$

where $E_{\text{red}}^0$ is the standard state reduction potential for the ferricyanide/ferrocyanide couple vs. Ag/AgCl (for the ferricyanide/ferrocyanide couple, $E_{\text{red}}^0 = 0.36$ V vs. SHE and $E_{\text{red}}^0 = 0.197$ V for Ag/AgCl vs. SHE; therefore $E_{\text{red}}^0 = 0.163$ V vs. Ag/AgCl), $R$ is the gas constant, $T$ is the temperature, $F$ is Faraday’s constant, $z$ is the number of electrons
transferred, $a_{red}$ is the activity of the reduced species, and $a_{ox}$ is the activity of the oxidized species. For an initial solution of nearly pure ferricyanide, the Nernst equation is used to obtain an $a_{red} \sim 0.43$ V (assuming $a_{red} > 0.9999$ and $a_{ox} < 0.0001$), in agreement with our measurements. As shown at Figure 2.10, the potential was found to rapidly decrease when the plasma was ignited and eventually reached a quasi steady-state value; higher discharge currents produced a larger potential drop. The decrease in the solution potential confirms that Fe(CN)$_6^{3-}$ is reduced to Fe(CN)$_6^{4-}$, and the steady-state potential suggests that the reduction occurs at a constant rate that is higher for higher discharge currents, which is in agreement with our UV–vis absorbance results. The interfacial region where the plasma contacts a liquid is fundamentally different than a metal–solution interface in a typical electrochemical system. In addition to the absence of surface sites for reactant species and reduction products to adsorb and accumulate, the edge of a plasma is characterized by a sheath with large electric field gradients that accelerate electrons to a surface [62]. This sheath potential should cause electrons to flow from the gas to the solution, analogous to the effect of the electrode potential at a

![Figure 2.10](image.png)

**Figure 2.10.** Solution potential measured as a function of time by a Pt probe placed at the plasma-liquid interface, with respect to an Ag/AgCl reference electrode. The solution potential was measured at two different discharge currents ($i_d$), 3 and 6 mA, every 10 seconds.
metal–solution interface. In order for reduction to occur, the donor and acceptor states in electron-transfer reactions such as this one must be of equal energy [63]. Since a plasma contains a complex distribution of electron energies, we propose that a fraction of the electrons with the appropriate energy reduce the Fe(CN)$_6^{3-}$ ions. The remaining electrons may be involved in other charge-transfer processes such as hydrogen formation, as indicated by the pH change in the cathode bath, leading to a lower than expected reduction of Fe(CN)$_6^{3-}$ molecules. In order to assess water electrolysis by the plasma, we measured the pH change in the catholyte bath. The half-cell reaction for water electrolysis that occurs at the cathode electrode (under acidic conditions) is:

$$\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2(\text{g})$$

and the relation between H$^+$ concentration and solution pH is:

$$\text{pH} = -\log(a^{\text{H}^+})$$

Thus, the pH change in the catholyte bath should provide an indication of H$^+$ reduction. The pH was obtained after plasma exposure using a digital pH meter (Accumet Basic Model AB15). The pH measurements are shown in Figure 2.11 and the calculations for

![Figure 2.11](image.png)

**Figure 2.11.** pH of the catholyte initially containing 0.2 mM ferricyanide and 0.1 M KCl in deionized water after plasma exposure for different times.


H⁺ reduction are shown in Table 2.4. Additional experiments are required to better understand and optimize electron transfer from the plasma to specific ionic species in the liquid – nonetheless, these experiments provide evidence of electron transfer reactions between a plasma discharge and aqueous ions to mediate electroreduction reactions in solution.

**Table 2.4.** pH change and H⁺ reduction as a result of plasma exposure. The catholyte solution initially contained 0.2 mM K₃Fe(CN)₆ and 0.1 M KCl in deionized water (pH~7.34).

<table>
<thead>
<tr>
<th>Current (mA)</th>
<th>Exposure Time (min)</th>
<th>Initial pH</th>
<th>Final pH</th>
<th># H⁺ initial</th>
<th># H⁺ final</th>
<th># H⁺ reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2</td>
<td>7.34</td>
<td>9.177</td>
<td>4.13E+14</td>
<td>6.01E+12</td>
<td>4.07E+14</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>7.34</td>
<td>9.900</td>
<td>4.13E+14</td>
<td>1.14E+12</td>
<td>4.12E+14</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>7.34</td>
<td>10.433</td>
<td>4.13E+14</td>
<td>3.33E+11</td>
<td>4.12E+14</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>7.34</td>
<td>10.660</td>
<td>4.13E+14</td>
<td>1.98E+11</td>
<td>4.13E+14</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>7.34</td>
<td>9.653</td>
<td>4.13E+14</td>
<td>2.01E+12</td>
<td>4.11E+14</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>7.34</td>
<td>10.417</td>
<td>4.13E+14</td>
<td>3.46E+11</td>
<td>4.12E+14</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>7.34</td>
<td>10.810</td>
<td>4.13E+14</td>
<td>1.40E+11</td>
<td>4.13E+14</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>7.34</td>
<td>11.080</td>
<td>4.13E+14</td>
<td>7.51E+12</td>
<td>4.13E+14</td>
</tr>
</tbody>
</table>
Application of plasma-liquid electrochemistry to Ir nanoparticle synthesis: Sensors are a class of devices that produce measureable response to changes in the chemical environment. For example, the detection of hydrogen peroxide (H$_2$O$_2$) is important to understanding the pathway of several enzymatic reactions [64, 65, 66, 67]. Recently, Ir nanoparticle-based sensors have been utilized as a biosensor for the amperometric detection of enzymatically generated H$_2$O$_2$ [68, 69]. One approach to preparing Ir nanoparticles is chemical synthesis [70]. The preparation of Ir nanoparticles in solution is amenable to solution processing such as screen-printing technique to fabricate thin film electrodes at low cost [68]. However, Ir is difficult to reduce [71] and toxic chemicals such as NaBH$_4$ are undesirable for biochemical applications. Here we present an alternative approach to Ir nanoparticle synthesis based on plasma electrochemical reduction – a plasma discharge is used to directly reduce aqueous Ir salts to metallic Ir nanoparticles. We then evaluate the amperometric response of the Ir nanoparticles for H$_2$O$_2$ detection.

In order to compare the plasma synthesized Ir nanoparticles with a reference material, we prepared Ir nanoparticles by standard chemical techniques [70]. Briefly, citric acid (10 mM, 0.84 ml) was added to IrCl$_3$·xH$_2$O (1.8 mM, 11.12 ml) solution and titrated with NaOH (100mM) to a pH of 7. NaBH$_4$ (10 mM, 8.4 ml) was slowly added and stirred overnight.

In this study, plasma electrochemical reduction of aqueous Ir salt was carried out in a Pyrex glass vessel (PYREX NO. 3140). The detailed experimental setup is described in Figure 1.3b. For TEM characterization, IrCl$_3$·xH$_2$O (1 mM, 20 ml) solution and IrCl$_3$·xH$_2$O (1 mM, 20 ml) solution with citric acid (0.4 mM) were reduced with 4 mA
current for 1 hour under 30 sccm of Ar flow rate. Other samples for characterization were prepared with IrCl$_3$·xH$_2$O (0.067 mM, 20 ml) solution and IrCl$_3$·xH$_2$O (0.67 mM, 20 ml) solution with citric acid (0.4 mM).

To confirm the morphology and crystalline structure of Ir nanoparticles, transmission electron microscopy (TEM) characterization was performed by using a Techai F300 at 300 kV. Representative TEM images of Ir nanoparticles synthesized by

![Representative TEM images and corresponding particle size distributions of Ir NPs prepared by (a) chemical synthesis with citric acid, (b) plasma electrochemical synthesis without citric acid, and (c) plasma electrochemical synthesis with citric acid.](image)

**Figure 2.12.** Representative TEM images and corresponding particle size distributions of Ir NPs prepared by (a) chemical synthesis with citric acid, (b) plasma electrochemical synthesis without citric acid, and (c) plasma electrochemical synthesis with citric acid.
chemical synthesis and plasma electrochemical synthesis without and with citric acid are shown in Figure 2.12. From the histograms, the average particle size for chemical synthesis and plasma electrochemical synthesis without citric acid is determined to be 2.2 nm. Plasma electrochemical synthesis with citric acid results in a much smaller average particle size (~1.5 nm). These results are explained by the role of citric acid which passivates the particles and reduces agglomeration. Interestingly, we find that the Ir nanoparticles synthesized by plasma electrochemical reduction exhibit a greater degree of crystallinity than those synthesized by chemical synthesis which appear to be amorphous. As we will show by XPS, we believe this is because of the presence of metal oxide (IrO₂).

To verify the reduction of aqueous Ir cations to metallic Ir, X-ray photoelectron spectroscopy (XPS) measurements were performed with a PHI Versa Prove XPS Microprobe with a monochromatic Al Kα (1486.6 eV) source. XPS is powerful technique that can determine the chemical states as well as the relative atomic concentration in as-grown material. Figure 2.13 shows high resolution XPS spectra of the Ir 4f region Ir nanoparticles prepared by chemical synthesis and plasma electrochemical synthesis without and with citric acid. XPS survey spectra showed that carbon and oxygen are present in all films. Lines at 60.30 and 63.20 eV correspond to the Ir 4f 7/2 and Ir 4f 5/2 states of metallic Ir, respectively [72]. For Ir nanoparticles prepared by plasma electrochemical synthesis without citric acid, the lines are slightly shifted to 60.40 and 63.30 eV, respectively. This small difference might be caused by IrO₂ [73]. In comparison, Ir nanoparticles prepared by plasma electrochemical synthesis with citric acid and chemical synthesis contained much more IrO₂ as indicated by the
large shift in the Ir 4f lines [71]. The existence of IrO$_2$ is also confirmed by survey spectra.

In order to determine if the oxide states were on the surface of the particles, the films were sputtered by an Ar ion beam. XPS spectra as a function of sputtering time for Ir nanoparticles prepared by chemical synthesis are shown in Figure 2.14. With increasing sputtering time, the Cl 2p from the Ir precursor and C 1s from citric acid are removed at early stage but the O 1s peak does not change [see Figure 2.14a]. This suggests that the Ir nanoparticles prepared by chemical synthesis are covered by Cl and C. Similar results are shown for Ir nanoparticles prepared by plasma electrochemical synthesis in Figures 2.15a and 2.16a. In contrast to the previous results, the Ir 4f peaks are found to shift to lower binding energies with increasing sputtering time. This indicates that in the case of Ir nanoparticles prepared by plasma electrochemical synthesis, the oxide is on the surface whereas in the case of chemical synthesis the oxide
is both on the surface and in the bulk of the material. We believe these results are also in agreement with our TEM observations.

The electrochemical characteristics of the Ir nanoparticles were evaluated by the amperometric response to H$_2$O$_2$. As-prepared solutions of Ir nanoparticles were dispersed in active carbon black powder Vulcan XC-72 (Cabot) and dried in an oven at 60°C. Afterwards, 8 mg of the electrocatalyst were dispersed in ethanol (200 µL) and Nafion solution (100 µL, 5 wt %) in an ultrasonic bath for 30 minutes. 8 µL of this solution was deposited onto a glassy carbon working electrode (0.5 cm in diameter, AFE2M050GC, Pine Instrument) and dried in ambient air for 3 minutes. During electrochemical measurements, the working electrode was operated at 900 rpm and an SCE reference electrode and Pt mesh (1cm×1cm) were used as the reference electrode.

Figure 2.14. XPS spectra collected from Ir nanoparticles with chemical synthesis as a function of Ar$^+$ sputtering time.
Figure 2.15. XPS spectra collected from Ir nanoparticles with plasma-assisted electrochemical synthesis without citric acid as a function of Ar\(^+\) sputtering time.

Figure 2.16. XPS spectra collected from Ir nanoparticles with plasma-assisted electrochemical synthesis with citric acid as a function of Ar\(^+\) sputtering time.
and counter electrode, respectively. CV scans and amperometric response were obtained at various concentrations of H₂O₂ in a phosphate buffer solution (PBS) of pH 7.4.

Figure 2.17 shows the amperometric response of Ir nanoparticles prepared by chemical synthesis and plasma electrochemical synthesis without and with citric acid. Ir nanoparticles prepared by plasma electrochemical synthesis without citric acid are found to produce approximately twice the response of Ir nanoparticles prepared by chemical synthesis. Citric acid was found to increase this response further; as shown by TEM, particles synthesized with citric acid were less agglomerated which may lead to improved catalyst activity.

![Graphs](image)

**Figure 2.17.** (a) Typical amperometric response of Ir nanoparticles by chemical synthesis, plasma electrochemical synthesis without citric acid, and plasma electrochemical synthesis without citric acid. (b) Current concentration of H₂O₂ calibration plots at +0.6V versus Ag/AgCl.
2.4 Summary

In summary, we have demonstrated that a gaseous electrode is capable of transferring electrons and inducing electrochemical reactions in solution such as ferricyanide reduction and nanoparticle synthesis. The reaction rate is found to depend intimately on discharge parameters (e.g., discharge current) which control the electron density (or flux) and energy distribution of electrons in the plasma. The absence of a solid electrode and the ability to tune the electron density, electron energy, and solution potential open a new direction for electrochemistry based on reactions between gas-phase electrons and ionic electrolytes such as tunable property of nanoparticles. Although there is no doubt that plasma electrochemistry is facile, cost-effective, and green, we believe there are additional advantages to reactions on surfaces to synthesize materials directly on a substrate. With this motivation, in the next three chapters, we focus on plasma electrochemical reactions at the interface of a plasma and a thin film.
CHAPTER 3
DIRECT WRITING OF PATTERNED METAL NANOPARTICLES

3.1 Introduction

The ability to initiate and control electrochemical reactions with a gaseous (i.e. plasma) electrode enables unique applications of plasma discharges. In the previous chapter, we showed that plasmas can reduce aqueous ions such as ferricyanide or metal salts. These reactions can also be performed at a gas-solid interface. In the case of metal nanoparticles, this would allow the material to be immobilized on a substrate for direct use in applications. In addition, if the reduction is performed locally, patterns of metal nanoparticles may be generated which is important for many applications of these novel materials (see Chapter 1). In this chapter, we show that metal nanoparticles can be generated by exposing films of metal cations dispersed in polymers to a plasma discharge. The electrons in the plasma interact and react with the supported metal cations to reduce them to crystalline metal nanoparticles. Plasma electrochemical reduction is clean (high purity) and versatile, allowing a wide-range of metal nanoparticles to be formed including Ag, Au, Pt, Ru, and Ir. By scanning a microscale plasma across the film, patterns of metal nanoparticles with a dimension of ~100 microns are produced. We demonstrate that the patterned metal nanoparticles generated by this approach are optically active, exhibiting surface plasmon resonance (SPR), and can be used as catalysts to selectively nucleate and control the growth of indium arsenide (InAs) nanowires.
3.2 Experimental details

*Materials*: Silver nitrate (AgNO₃; Fisher Scientific), chloroauric acid trihydrate (HAuCl₄·3H₂O; Sigma-Aldrich), chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O; Sigma-Aldrich), ruthenium chloride (RuCl₃; Sigma-Aldrich), and iridium chloride (IrCl₃; Sigma-Aldrich) were used as metal salt precursors. Polyvinyl alcohol (PVA, MW=100000) and poly(methyl methacrylate) (PMMA, PERSPEX® CP-80) were supplied by MP Biomedical, LLC and Lucite International Inc, respectively.

*Formation of patterned films of metal nanoparticles*: A direct-current (dc), atmospheric-pressure microplasma jet was formed between a stainless-steel capillary tube (I.D. = 180 μm, Restek, Inc.) and a grounded counter electrode (Si substrate) using a negatively-biased high voltage power supply (Keithley, Inc. Model 246). Argon (Ar) gas flow was coupled to the tube electrode and controlled by a mass flow controller (MFC). To ignite the microplasma, a high voltage (∼ 2 kV) was applied. The plasma was then stabilized at constant current by a ballast resistor (R = 160 k Ω) and adjusting the power supply voltage. The moving stage controlled by a pair of numerically-controlled stepping motors was used to move the substrate in the x and y directions. The step size for the scanning was 1 mm and the scanning rate could be adjusted between 3 and 30 mm min⁻¹ by changing the delay time between steps. The z direction was also controlled by a third stepping motor which fixed the distance between the tube and counter electrode. To form patterns of metal nanoparticles, the same solutions of metal precursor and polymer were prepared as films on Si substrates by drop casting or spin coating. The thin films were exposed to a scanning microplasma to produce microscale patterns of metal
nanoparticles. The patterning technique was optimized by varying several experimental parameters including discharge current (50 µA~8 mA), scanning rate (3 mm/min~30 mm/min), and Ar flow rate (30 sccm ~ 150 sccm).

**InAs nanowire growth:** InAs nanowires were synthesized using a previously reported chemical vapor deposition (CVD) system [74]. Briefly, InAs powder (Alfa Aesar) was thermally evaporated at 680 °C in a horizontal tube furnace under vacuum (pressure ca. 1.5 Torr). The In and As vapor were transported downstream by 30 sccm Ar/H2 carrier gas to a substrate. The substrate was placed 5 cm from the powder source. To prepare the patterned Au nanoparticles, a solution of HAuCl4 and PMMA were spin coated and scanned by a microplasma at a rate of 9 mm/min across the film surface. The film was then developed in acetone in order to remove the unexposed polymer. Nanowires were grown with the Au catalysts following the vapor-liquid-solid (VLS) growth mechanism [75].

**Ultraviolet–visible absorbance spectroscopy (UV–vis):** UV-vis spectra were obtained at room temperature with a Shimadzu UV-1800 spectrometer. Solutions of nanoparticles were prepared by dissolving 1 mM AgNO3 or HAuCl4 with 1 wt% PVA in water and reducing with a microplasma operated at 30 sccm Ar and 8 mA DC current for 1 minute. Thin films of nanoparticles dispersed in polymer were obtained by drop casting 0.7 ml of solution containing 50 mM AgNO3 or HAuCl4 and 3 wt% PVA in water onto a 1.5×3 cm Si wafer and scanning a microplasma at a rate of 30 mm/min across the film surface (30
sccm Ar, 0.2 mA DC current). A film area of approximately 2.5×1 cm was reduced for absorbance measurements.

**X-ray diffraction (XRD):** XRD characterization was performed with a Scintag X-1 advanced X-ray diffractometer with Cu Kα radiation (λ = 0.154178 nm) at a scanning rate of 0.004 degree per second. To avoid overlap of peaks with the reduced metal precursor, p-type Si (111) was used as the substrate. Samples were prepared by drop casting a 160 mM solution of a metal precursor (AgNO₃, HAuCl₄, H₂PtCl₆, IrCl₃, or RuCl₃) and 10 wt% PVA onto the substrate and drying overnight. Then, nanoparticles were formed by scanning the microplasma at 9 mm/min (4 mA~8 mA discharge current, 150 sccm Ar). Spectra from an unexposed area were compared to the reduced region.

**Scanning electron microscopy (SEM):** SEM images of patterned films of metal nanoparticles were obtained with a Hitachi S4500 operated at 10 kV. Samples for SEM were prepared by spin coating solutions composed of 1 mM AgNO₃ and 10 wt% PVA at 3000 RPM and scanning a microplasma at a rate of 9 mm/min across the film surface (4 mA discharge current, 150 sccm Ar). We also prepared films in PMMA by spin coating a solution of 10 mM AgNO₃ and 5 wt% PMMA in acetone and scanning a microplasma at a rate of 9 mm/min across the film surface (200 µA discharge current, 30 sccm Ar). In this case, the film was developed in acetone to remove the unexposed PMMA.

**High resolution transmission electron microscopy (TEM):** TEM was performed with a Philips Tecnai F30 operated at 300 kV. To prepare metal nanoparticle samples for TEM,
metal precursors (AgNO\textsubscript{3}, HAuCl\textsubscript{4}, H\textsubscript{2}PtCl\textsubscript{6}) were dispersed at different concentrations (1-160 mM) in 10 wt% of PVA in water, spin coated at 3000 RPM onto a Si substrate, and patterned by scanning a microplasma at a rate of 9 mm/min across the film surface (4 mA discharge current, 150 sccm Ar). The films were then redissolved in water, sonicated for 40 min, and deposited onto carbon-coated copper TEM grids (Ted Pella, Inc.) by dip coating and drying.
3.3 Results and discussion

In the course of developing and optimizing our patterning technique, we explored two approaches to plasma electrochemical reduction of metal precursors: 1) solutions of metal salt and polymer were directly reduced by a microplasma to form colloidal (i.e. suspended) metal nanoparticles or, alternatively, 2) the same solutions of metal salt and polymer were spin coated onto a substrate and dried to obtain a thin film, then reduced by a scanning microplasma to form patterns of metal nanoparticles. To reduce metal precursors in solution, aqueous solutions of metal salt and water-soluble polymer [e.g. polyvinyl alcohol (PVA)] were prepared [Figure 3.1a] and exposed to a microplasma operated as the cathode of an electrochemical cell, with a Pt foil as the anode [Figure 3.1b]. As current flowed through the bath, the metal cations were reduced by the microplasma to nucleate metal nanoparticles in solution. The presence of polymer in solution prevented uncontrolled particle growth and aggregation of the metal nanoparticles [46]. Figure 3.1(c) shows photos of colloidal Ag (top) and Au (bottom) nanoparticles, after plasma electrochemical reduction of solutions of AgNO$_3$/PVA and HAuCl$_4$/PVA, respectively. During operation of the microplasma, the solution samples showed a significant change in color; the AgNO$_3$/PVA solution went from colorless to yellow, whereas the HAuCl$_4$/PVA solution turned from yellow to pink. These color changes, which are indicative of the unique optical properties of Ag and Au (discussed in more detail later), confirm that metal cations were reduced by the microplasma to metal nanoparticles.

To generate patterns of metal nanoparticles, we adapted the synthesis methodology used to prepare colloidal metal nanoparticles. Thin films of well-dispersed,
Figure 3.1 Illustration of the two approaches employed for synthesis of metal nanoparticles with polymers. Metal nanoparticles were prepared in solution by (a) dissolving a metal salt precursor with polymer in water, (b) exposing to a microplasma operated as the cathode of an electrochemical cell and (c) directly reducing in solution. Alternatively, free-standing, transparent, flexible films of patterned metal nanoparticles were fabricated by (d) spin-coating and drying the same initial solution of metal salt precursor and polymer as in (a) onto a Si substrate, (e) exposing to a rastered microplasma, and (f) removing from the substrate.
supported metal cations were obtained by spin coating the same starting solutions of metal salt and polymer previously described [Figure 3.1d]. The metal cations were then reduced by the microplasma with an electrical circuit similar to that in liquid [see Figure 3.1b] except that a Si substrate was operated as the anode [Figure 3.1e]. In contrast to experiments with liquids, the nanoparticles were formed as a pattern, since the microplasma could be scanned across the film surface and the particles were immobilized by the polymer matrix. In the top of Figure 3.1f, we demonstrate that arbitrary patterns such as our university name "CWRU" can be created by this method. In addition, the polymer films can be removed from the substrate with the metal nanoparticles intact to produce flexible, transparent films of patterned nanoparticles [see bottom of Figure 3.1e].

To characterize the metal nanoparticles synthesized by plasma electrochemical reduction, we employed a variety of analytical techniques. Metal nanoparticles of Ag and Au exhibit a well-known surface plasmon resonance (SPR) band that can be detected by UV-Vis spectra. Figures 3.2a and b shows absorbance spectra for various samples prepared in solution and as a thin film by microplasma reduction of AgNO₃ or HAuCl₄ (in PVA), respectively. For AgNO₃ reduction, an intense band was detected at ~425 nm in the thin film sample and ~410 nm in the solution sample, both of which closely correspond to the SPR band of Ag nanoparticles [Figure 3.2a]. During the experiment, this band was observed to increase in intensity with plasma current as a result of faster reduction. In the case of HAuCl₄ reduction, a band appears at ~580 nm for the thin film sample, as compared to ~530 nm for the solution sample, which both approximately agree with the SPR band of Au nanoparticles [Figure 3.2b]. Spectra for thin film samples consistently show a red shift of the plasmon peak compared to spectra for liquid samples.
The SPR band for noble metal NPs is a function of particle size, shape, and overall morphology. In particular, when particles aggregate, the absorbance spectra show several distinct characteristics: 1) the peak intensity will decrease due to depletion of stable nanoparticles; 2) the peak will broaden due to a change in the optical scattering mode; and 3) a change will occur in the color of solutions. For example, unagglomerated Au nanoparticles exhibit a pinkish or reddish color when well dispersed, whereas agglomerated Au nanoparticles appear bluish or purplish. Based on this analysis, we suggest that our observed red shift is due to particle aggregation in the films [76].

**Figure 3.2** (a) UV-vis absorbance spectra of Ag nanoparticles synthesized in solution (solid line) and in polymeric thin films (dotted line) by microplasma reduction of AgNO₃/PVA. (b) UV-Vis absorbance spectra of Au nanoparticles synthesized in solution (solid line) and in polymeric thin films (dotted line) by microplasma reduction of HAuCl₄/PVA. (c) Solutions of AgNO₃/PVA before and after exposure to a microplasma (color change indicates reduction of Ag⁺ to colloidal Ag nanoparticles). (d) Thin films of AgNO₃/PVA before and after microplasma reduction (color change indicates reduction of Ag⁺ to Ag nanoparticles).
believe the red shift is larger for Au than Ag because the Ag precursor is reduced at a higher rate than the Au precursor [77] and the difference in agglomeration between the solution and film is more pronounced for Au nanoparticles. The presence of metal nanoparticles was also confirmed by the visual color change – solutions and films of AgNO₃/PVA went from colorless to yellow brown [see Figure 3.2c-d, respectively].

The reduction of metal precursors from metal cations to crystalline metal in thin films was verified by XRD characterization. A representative XRD spectrum for AgNO₃/PVA thin films after plasma reduction shows several intense, broad peaks, suggesting that AgNO₃ was reduced to crystalline Ag nanoparticles [Figure 3.3a]. The diffraction peaks at 38.1°, 44.2°, 64.4°, and 77.4° can be ascribed to the Ag(111), Ag(200),

![Figure 3.3 XRD spectra of (a) Ag, (b) Au, (c) Pt, (d) Ir, and (e) Ru nanoparticles synthesized by microplasma reduction of the corresponding metal salt precursors in polymeric thin films. Spectra from an area of the film not exposed to the microplasma is also shown in (a) for comparison.](image)
Ag(220) and Ag(311) respectively, and indexed to the fcc (face centered cubic) crystalline phase of Ag (JCPDS file 87-0597). The corresponding lattice spacings calculated from Bragg’s law are 2.359Å, 2.043Å, 1.444Å, and 1.232Å. We also collected XRD spectra from regions of the film that were not exposed to the microplasma and found no discernible diffraction peak signals [see Figure 3.3a]. XRD characterization was similarly carried out for thin films of other metal precursors (in PVA) including HAuCl₄ [Figure 3.3b], H₂PtCl₆ [Figure 3.3c], IrCl₃ [Figure 3.3d], and RuCl₃ [Figure 3.3e]. The XRD patterns match up closely to reported data for these materials: (JCPDS fine 04-0784: Au), (JCPDS fine 04-0802: Pt), (JCPDS fine 06-0598: Ir),

Figure 3.4 (a) SEM image of patterned thin films of metal nanoparticles prepared by microplasma reduction of AgNO₃/PVA. A higher magnification images is shown in (b). (c) Image of patterned thin film of metal nanoparticles prepared by microplasma reduction of AgNO₃/PMMA and subsequent removal of unpatterned area by dissolving in acetone. A higher magnification image is shown in (d).
and (JCPDS fine 06-0663: Ru), respectively. In contrast to previously reported results for plasma reduction, no thermal annealing was necessary to obtain crystalline material [58].

The reduced films were imaged by SEM to determine the size (i.e. line width) of our transferred patterns and the size, shape, and overall morphology of as-synthesized nanoparticles within the patterns. Figure 3.4a shows an image of a thin film of AgNO$_3$/PVA after scanning a microplasma across its surface at a rate of 9 mm/min. The transferred line has an overall width of approximately 150 μm and is comprised of two regions. Near the center of the line, there is a high density of particles and towards the edges, the density of particles decreases. We believe the plasma density is not uniform (in the radial direction) and the exposed film is reduced at different rates. The overall width of the transferred line appears to be close to the size of the microplasma. At higher magnification (Figure 3.4b), the SEM image clearly show that the patterns are composed of smaller particles. The particles appear to be slightly agglomerated, but uniformly distributed in the patterned area [see inset of Figure 3.4b]. In addition to PVA, we have also explored other polymers to compare and optimize the patterning process. For example, polymers such as poly(methylmethacrylate) (PMMA) are known to chemically change when exposed to plasmas and/or electron beams [78,79]. We have found that the unexposed region of a PMMA film can be selectively removed by acetone [80], leaving behind patterned metal nanoparticles on a clean substrate. Figures 3.5c-d shows representative SEM images of a thin film of AgNO$_3$/PMMA whereby optimizing some of these parameters, a line pattern with a width of ~30 μm was generated which is significantly smaller than the size of the microplasma. The acetone treatment may have removed some of the film exposed to the microplasma, reducing the overall pattern size.
In addition, while optimizing our patterning process for films of AgNO$_3$/PMMA, we observed the following empirical relationships: lower plasma currents, higher scanning rates, and thinner films (i.e. higher spin coating rates) yielded smaller line widths [see Figure 3.5].

In order to image individual nanoparticles contained in the films, TEM was performed. Samples were prepared by re-dissolving the reduced thin films in water and drop casting the dispersions on carbon-coated copper TEM grids. Figures 3.6a-c show

![Figure 3.5](image)

**Figure 3.5** SEM images of patterned metal nanoparticles prepared by plasma electrochemical reduction of AgNO$_3$/PMMA thin films. Scanning rates of 3 mm/min (a) and 9 mm/min (b) at 50 μA discharge current and 30 sccm Ar were used with films spin coated at 3000 RPM. Alternatively, a discharge current of 0.2 mA (c) and 5 mA (d) was used at 30 sccm Ar and 9 mm/min scanning rate with films spin coated at 3000 RPM. We also tried films spin coated at 3000 RPM (e) and 500 RPM (f) at 200 μA discharge current, 9 mm/min scanning rate, and 30 sccm Ar.
Figure 3.6 TEM images of (a) Ag, (b) Au, and (c) Pt nanoparticles synthesized by microplasma reduction of 160 mM AgNO₃, 160 mM HAuCl₄, and 160 mM H₂PtCl₆, respectively, in PVA. The influence of the initial metal precursor concentration is shown in (d) 160 mM of AgNO₃ and (e) 1 mM of AgNO₃.

Figure 3.7. Histograms of particle size distributions for plasma electrochemical reduction of films containing (a) 1 mM and (b) 160 mM AgNO₃ in PVA (after redissolving films in water and drop casting onto TEM grids).
representative TEM images of nanoparticles synthesized in thin films from AgNO₃, HAuCl₄, and H₂PtCl₆, respectively. Ag nanoparticles are found to be unagglomerated, spherical, and crystalline with an approximate diameter of 20 nm. The lattice spacings observed by TEM correspond well with the (111) and (200) crystalline planes of fcc Ag, respectively, in agreement with XRD results. In comparison, Au NPs are approximately 5 nm in diameter (Figure 3.6b) with lattice spacings of 1.442Å and 1.230Å which correspond to the (220) and (311) crystalline planes of fcc Au, respectively. Similarly, Pt NPs are approximately 5 nm in diameter and we observe a lattice spacing of 1.388Å which corresponds to the (220) crystalline plane of fcc Pt [Figure 3.6c].

To understand the mechanism for particle nucleation and growth, we varied the metal salt precursor concentration in the thin films for the AgNO₃/PVA system [see Figure 3.8]. At lower precursor concentrations (1 mM of AgNO₃), the particle size were found to be nearly spherical with an average size 34.0 nm [Figure 3.6a]. At higher precursor concentrations (160 mM of AgNO₃), the Ag NPs were decreased to 19.8 nm [Figure 3.7b]. Interestingly, at these concentrations we observed the presence of highly faceted, shaped nanoparticles. Overall, these results appear to follow classical nucleation theory [81] and provide some insight into the growth mechanism. When the precursor concentration is high, the minimum supersaturation required for particle nucleation is reached at various spatial positions in the film, driven by plasma reduction, and a relatively large number of smaller particles are formed. At low precursor concentration, nucleation events may be suppressed, except in a few positions in the film where supersaturation is reached, and a relatively small number of larger particles are formed. These particles then grow, by addition of metal precursor, into large, shaped
Figure 3.8 A control experiment is demonstrated: (a)-(c) the microplasma is formed directly with the film to reduce the metal salt precursor to crystalline metal nanoparticles; (d)-(f) a grounded mesh is placed between the microplasma and the film to block the electrons and the film shows no change (i.e. no reduction of the metal salt precursor).

nanoparticles. By controlling the precursor concentration, it is then possible to influence the particle growth mechanism and control the size and shape [82].

Despite this dependence on precursor concentration, the mechanism for particle nucleation remains unclear because of the nature of the plasma reduction process. Plasmas are characterized by a complex physiochemical environment that includes the presence of electronically-excited atoms and molecules, charged species (e.g. ions and electrons), UV and VUV light, and hot gases that can transfer thermal energy. Many of these types of interactions have been previously used to reduce metal salts in polymers including electron beams [83,84,85], UV [82,86] or vacuum UV irradiation [87], and heating [88,89,90]. Although the reduction process has been successfully carried out by a microplasma, a key question is which of these aforementioned processes is responsible?
To answer this question, we designed a control experiment that can effectively eliminate some of the ambiguity. As shown in Figure 3.8a, normally, the microplasma is formed between the tube electrode and the film that contains the metal salt precursor. By placing a grounded mesh between the microplasma and the film, the electrons could be blocked and kept from interacting and reacting with the metal precursor [see Figure 3.8b]. On the other hand, UV radiation and hot gases can still penetrate through the mesh and interact with the film. The images in Figure 3.8c-d shows that the microplasma is formed in an identical fashion in both cases. However, when the samples are removed, it is clear that the grounded mesh prevents reduction of the metal salt and nanoparticle formation [Figure 3.8e and f]. We believe this clearly shows for the first time that electrons in a plasma are responsible for reduction of supported metal cations [58].

**Figure 3.9.** (a) SEM image of InAs nanowires grown on patterned Au nanoparticles prepared by plasma electrochemical reduction of a film containing 50 mM HAuCl$_4$/5 wt% PMMA. Inset shows patterned film of Au nanoparticles before nanowire growth. (b) High magnification image of patterned InAs nanowires. High magnification image of patterned area (c) and border between patterned area and unpatterned area (d) are also shown.
A potential application of patterned metal nanoparticle films is the catalytic growth of semiconductor nanowires. Recently, InAs nanowires have been actively explored as a channel material for high performance transistors owing to their high electron mobility and ease of ohmic metal contact formation [91]. Furthermore, InAs nanowire-based transistor devices have potential applications in gas sensing due to the presence of rich surface states [74]. An important issue for scalable applications is controlled and reproducible growth of the InAs nanowires in terms of their spatial position, size, and shape [92]. As proof-of-concept, we have carried out catalytic growth of InAs nanowires on patterned films of Au nanoparticles prepared by plasma electrochemical reduction. As shown in Figure 3.9a and b, we are able to catalyze the growth of InAs nanowires on selective areas where Au nanoparticles were formed by the reduction process. The nanowires were found to be high quality, with diameters of approximately ~200 nm and lengths of 3-5 µm [Figure 3.9c]. The relatively large diameter of the nanowires as compared to the individual nanoparticles [see Figure 3.6]
may be caused by particle agglomeration; smaller diameter nanowires can be grown by lowering the initial metal precursor concentration which limits agglomeration [see Figure 3.10]. Nonetheless, the nucleation and growth of the nanowires is highly selective, leaving a clear boundary between the areas that contained Au nanoparticles and the bare substrate [Figure 3.9d and Figure 3.10].
3.4 Summary

In this chapter, direct writing of patterned films of metal nanoparticles via plasma electrochemical reduction has been presented. A microscale plasma is scanned across the surface of a film containing metal precursor in a polymer matrix to electrochemically reduce the metal cations to crystalline metal nanoparticles. The technique is generic and can be applied to a range of different metal precursor/polymer systems. Since the plasma is operated continuously at atmospheric pressure, the approach is amenable to roll-to-roll processing and should enable low-cost, high-throughput fabrication of patterned metal nanoparticles in flexible, transparent films, making it potentially useful for plasmonic and catalytic applications.
CHAPTER 4
EXTRACTION OF A LOW-CURRENT DISCHARGE AT AMBIENT CONDITIONS FOR LITHOGRAPHIC NANOSCALE PATTERNING

4.1 Introduction

In the previous chapter, we have demonstrated that plasmas can locally reduce metal ions in polymeric films to directly write patterns of metal nanoparticles [93]. A drawback of this approach is that direct exposure of a polymer film to a microplasma could result in damage due to heating and sputtering. In addition, the resolution of our patterns was limited to $\sim 10 - 100 \, \mu m$, because of the size of the plasma source. An alternative approach to patterning would be to use a remote plasma such that direct interaction of all the energetic species with the polymer is avoided. The electrons could be extracted since they are primarily responsible for the reactions at the surface (i.e. metal ion reduction) by biasing the substrate. Combining the extracted discharge with lithography would lead to the transfer of patterns into a film. In this chapter, we characterize a low-current discharge that is extracted from a microplasma to serve as a source of electrons at ambient conditions for nanopatterning applications. Our idea is based on the generation of electron beams from hollow cathode discharges where a positively-biased electrode is used to extract and accelerate electrons [94]. A key difference is that we extract the electrons at higher pressures, which leads to ionization and the formation of a weakly-ionized discharge due to collisions with the background gas atoms [61]. Nonetheless, the discharge contains electrons which can be accelerated to a surface to reduce metal ions and, unlike the primary microplasma, can be sustained at
very low currents (<1 mA), thus mitigating heating and sputtering of the exposed film. Overall, our strategy allows nanopatterns with spatial resolution of ∼100 nm to be produced at ambient conditions.
4.2 Experimental details

Thin film preparation: Silver nitrate (AgNO$_3$) and polyvinyl alcohol (PVA; MW=100000) were purchased from Fisher Scientific and MP Biomedical LLC, respectively. To prepare a thin film, 2 wt% PVA was first dissolved in a mixture of ethanol-water (1:1) at room temperature. Then, 10 mM of AgNO$_3$ was added to the solution. Finally, the AgNO$_3$/PVA solution was spin coated on a Si substrate at 3000 rpm for 3 minutes and dried in air overnight.

Alumina membrane template: Porous alumina membrane templates were purchased from Synkera Technologies (Longmont, CO). The templates were 1 cm × 1cm and 50 µm thick. Two different pore diameters were investigated: 35 ± 2 nm and 150 ± 10 nm. The 35 nm and 150 nm templates contain approximately 1×10¹⁰ pores/cm$^2$ and 4 × 10⁹ pores/cm$^2$, respectively.

Operation of extracted discharge: Argon (Ar) gas flow was coupled to a metal capillary tube and controlled by a mass flow controller (MFC). To ignite the main microplasma, a negative high voltage (~2 kV) was applied between the capillary tube and a metal (stainless steel) mesh. The microplasma current was stabilized by a ballast resistor (R=160 kΩ) and adjusted by the negative power supply voltage. A low-current discharge was extracted by placing a third electrode downstream of the metal mesh and biasing with a positive high voltage (~5 kV). All voltages in our set up were monitored by electrical probes. The microplasma and extracted discharge current were obtained from the voltage drop across a 500 Ω resistor and a 1 MΩ resistor, respectively.
**X-ray photoelectron spectroscopy (XPS):** XPS characterization was performed with a PHI Versa Prove XPS Microprobe equipped with a monochromatic Al Kα (1486.6 eV) source. Samples were prepared by exposing our metal precursor loaded films to the extracted discharge for different times.

**Scanning electron microscopy (SEM):** SEM characterization was carried out with a Hitachi S4500 operated at 5 kV. To prepare SEM samples, our metal precursor loaded films were exposed to an extracted discharge with the alumina template mask. The films were then immersed in deionized (DI) water for 3 minutes to remove the unexposed regions and dried with N₂ gas.
### 4.3 Results and discussion

Figure 4.1a schematically depicts the low-current discharge extraction system. An atmospheric-pressure microplasma was ignited and sustained in Ar gas (flow rate = 150 sccm) between a stainless-steel capillary tube (Restek, Inc., I.D. = 180 μm, L = 5 cm) cathode and a metal grid anode by a negatively-biased high voltage direct current (dc) power supply. The microplasma current was controlled after gas breakdown by a

![Figure 4.1a](image_url)

**Figure 4.1** (a) Schematic diagram of the extracted discharge system consisting of a microplasma and a positively-biased third electrode. The resistor network was used to measure the I-V characteristics of the microplasma ($i_{\text{microplasma}}$, $V_{\text{microplasma}}$) and the extracted discharge ($i_{\text{ed}}$, $V_{\text{ed}}$). Photo corresponds to extracted discharge current of 800 μA and extraction electrode gap distance ($d_{\text{ee}}$) of 0.5 cm. (b) Process flow diagram for generating nanoscale patterns with extracted discharge consisting of the following steps: 1) spin coating of AgNO₃/PVA blend on Si substrate, 2) masking of discharge with alumina membrane template, and 3) removal of unexposed area by dissolving in deionized water for 30 s.
ballast resistor \( (R_1 = 160 \, \text{k}\Omega) \) and adjusting the power supply voltage. A 500 \( \Omega \) resistor \( (R_2) \) between the anode and ground was used to continuously monitor the microplasma current \( (i_{\text{microplasma}}) \). To extract a low-current discharge from the primary microplasma, a third electrode, consisting of a 3 cm \( \times \) 3 cm stainless steel plate, was positioned near the anode and positively biased with a separate high voltage dc power supply. The voltage on the extraction electrode could be varied between 0 and +15 kV, but was kept below the threshold for air breakdown (\( \sim 30 \, \text{kV/cm} \)) in all experiments. The distance between the anode and extraction electrode \( (d_{\text{ee}}) \) was varied with a micrometer and the collection area for the extracted discharge was fixed to 1 cm\(^2\) by using insulating tape. The extracted discharge current \( (i_{\text{ed}}) \) was obtained by measuring the voltage drop

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**Figure 4.2** (a) \( I-V \) characteristics of the microplasma. (b) \( I-V \) characteristics of the extracted discharge at various extraction electrode gaps \( (d_{\text{ee}}) \) [microplasma current=4 mA]. (c) Extracted discharge current as a function of microplasma current at various extraction electrode gaps \( (d_{\text{ee}}) \) [extraction voltage=3.1 kV]. (d) Electric field of extracted discharge in various extracted discharge current.
across a 1 MΩ resistor ($R_3$) with a homemade high voltage attenuator (1/1000) and the extracted discharge voltage was measured by the voltage difference ($V_{ed}$) between the microplasma anode and the extraction electrode. To transfer patterns, a masked, spin-coated film containing metal ions (e.g., Ag⁺) and polymer (e.g., PVA) was placed on the extraction electrode and exposed to the extracted discharge [Figure 4.1b].

We initially studied the electrical properties of the extracted discharge. I-V characteristics were obtained as a function of the following parameters: $V_{ed}$, $d_{ee}$, and $i_\text{microplasma}$. I-V characteristics of the microplasma and extracted discharge are shown in Figure 3.2a and 2b, respectively. While the microplasma could only be sustained at currents of 3 mA or higher, below which the microplasma extinguished, the extracted discharge could be sustained at significantly lower currents. The extracted discharge current increases with $V_{ed}$ without significantly disturbing the microplasma at the range of conditions explored here. For $i_{ed} < 300 \, \mu$A, $i_\text{microplasma}$ does not noticeably change. At higher values of $i_{ed}$ (300–1000 $\mu$A), $i_\text{microplasma}$ is found to decrease by less than 5%. As $d_{ee}$ is increased, a higher extraction voltage is required to produce a given discharge current [See Figure 4.3]. For example, in order to extract 200 $\mu$A at $d_{ee} = 0.3$ cm, the extraction voltage must be ~1.4 kV; to maintain the same current at $d_{ee} = 1.0$ cm, the extraction voltage must be increased to ~8.1 kV. As the microplasma current is increased, the extracted discharge current increases proportionally [Figure 4.2c]. This confirms that the microplasma is a source of electrons and increasing the electron density in the source allows more electrons to be extracted [95]. We note that when the microplasma was turned off, virtually no current could be measured at the extraction electrode (<1 $\mu$A) in the range of $V_{ed}$ explored here.
Overall, the I-V characteristics of the extracted discharge are significantly different than other atmospheric-pressure plasma sources, including the primary microplasma [59]. At high pressures (e.g., atmospheric), it is normally difficult to sustain a plasma at low currents because of collisional quenching of the electron population. When the current is increased to enhance ionization, the plasma may be unstable because of the glow-to-arc transition [61], and gas heating and sputtering become problematic. In comparison, the extracted discharge is sustainable at atmospheric pressure and low currents, as confirmed by the uninterrupted, nonlinear region of the I-V curves in Figure 4.2b. At higher discharge currents, gas breakdown most probably occurs as indicated by the constant voltage, resulting in a discharge with similar properties to other atmospheric-pressure plasmas. Our interest is in the low current regime which is characterized by

Figure 4.3 Microplasma current as a function of extracted discharge current. Microplasma current was initially set 4mA and then monitored by changing extracted discharge current.
weak ionization of the background gas. Assuming the gas is Ar, we can estimate the electron density \((n_e)\) in the extracted discharge by the following expression,

\[
n_e = \frac{j}{\mu_e E e}
\]

where \(E\) is the electric field, \(j\) is current density, and \(\mu_e\) is the electron mobility, assumed to be \(0.33 \times 10^6 \text{ cm}^2 \text{ Torr/Vs}\) for Ar [62]. If we assume a cross sectional area of 1 cm\(^2\), the electron density for the extracted discharge is on the order of \(10^7 \text{ cm}^{-3}\) to \(10^9 \text{ cm}^{-3}\), depending on \(V_{ed}, d_{ee}, \text{etc.}\); in comparison, the electron density in Ar microplasmas has been measured to be on the order of \(10^{15} \text{ cm}^{-3}\) [61]. Potential sources of error in this calculation include the presence of air, variations in the electric field due to sheath effects, and inaccuracies in our estimation of the discharge area. Further studies are required to fully understand the properties of the extracted discharge. Nonetheless, the

Figure 4.4. Photos of extracted discharge at electrode gaps of (a) 0.3 cm and (b) 0.5 cm as a function of indicated current (\(i_{ed}\)) and voltage (\(V_{ed}\)). The microplasma was operated at a constant current of 4 mA. The scale bar is 0.5 cm.
difference in electron densities between the extracted discharge and the microplasma is illustrated by this simple calculation.

Figure 4.4 shows images of the extracted discharge at various operating conditions. In Figure 4.4a, emission from the extracted discharge is clearly visible as the discharge current is increased to approximately 500 μA (i.e., as extraction voltage is increased). As $d_E$ is increased from 0.3 to 0.5 cm, the emission from the discharge is similar if the current is kept the same by increasing the extraction voltage [Figure 3.4b]. These observations indicate that higher extraction voltages lead to higher discharge currents as a result of enhancement of electron-impact ionization, in good agreement with the I-V measurements. We note that although a discharge is not visible at lower currents, a weakly-ionized discharge still exists that contains electrons, as well as some ions and other excited states (e.g., radicals).

Figure 4.5 XPS spectra of Ag 3d peaks in AgNO$_3$/PVA films after exposure to extracted discharge. The discharge was operated at 200 μA with an extraction voltage of 3.1 kV.
Films containing Ag⁺ were exposed to an extracted discharge and characterized by XPS to confirm the change in valence state as a result of electrochemical reduction. Figure 4.5 shows XPS spectra of films of AgNO₃/PVA (2 wt. %) exposed to an extracted discharge for various times. The XPS spectrum of the initial (unexposed) AgNO₃/PVA film shows peaks at 366.7 eV and 372.8 eV which can be assigned to Ag 3d₅/₂ and Ag 3d₃/₂, respectively. The binding energies of the peaks are slightly shifted from Ag ions, characteristic of Ag ions bound to alcohol groups in PVA [96]. With increasing exposure time, the respective peaks shift to higher binding energies of 367.8 eV and 373.9 eV, confirming reduction to Ag⁰ [97,98,99]. After 10 mins of exposure, the peaks no longer shift, confirming that the reduction is complete. We also performed XPS survey scans to evaluate atomic percentage as a function of exposure time. Table 4.1 show that the relative Ag content increases after plasma exposure, while the relative C content and the relative O content decrease and increase, respectively, after plasma exposure. We believe all of these changes are due to Ag reduction (which increased the relative Ag content in the film).

**Table 4.1** Atomic ratio of Ag 3d, C 1s, and O 1s.

<table>
<thead>
<tr>
<th>Exposure time</th>
<th>Ag3d (%)</th>
<th>C1s (%)</th>
<th>O1s (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>1.7</td>
<td>67.2</td>
<td>37.2</td>
</tr>
<tr>
<td>5 min</td>
<td>6.8</td>
<td>47.2</td>
<td>45.5</td>
</tr>
<tr>
<td>10 min</td>
<td>7.0</td>
<td>10.2</td>
<td>82.8</td>
</tr>
<tr>
<td>30 min</td>
<td>8.7</td>
<td>1.9</td>
<td>89.4</td>
</tr>
</tbody>
</table>
In order to produce a nanopattern, we incorporated a porous alumina template [Synkera Technologies, 150 nm pore size, Figure 4.6] into our reduction process [see Figure 4.1b, middle panel]. After exposing the masked film to the extracted discharge, the film was rinsed in deionized water for 30 seconds to remove the unexposed polymer [21]. We found that this step was necessary to avoid excessive charging of the polymer and obtain clear SEM images of the patterned film. SEM images of patterned films are shown in Figures 4.7a, 7b, 7c. For the 150 nm template, patterned Ag with dimensions of 150 nm are visible after 10 mins of exposure [Figure 4.7a]. A longer exposure time (30 mins) leads to a higher density of patterned Ag and a small increase in the pattern resolution [Figure 4.7b]. Smaller scale patterns were achieved by using low current; patterns with sizes as small as 150 nm were successfully transferred [Figure 4.7c]. However, the density of patterned Ag was significantly lower. This may be caused by the inability of electrons to pass through the pores at low current. Future studies are planned to optimize the mask geometry for nanoscale pattern transfer.

We also studied the transfer of patterns by scanning the extracted discharge at a constant rate across a film surface. This approach has potential for large area pattern
A moving stage controlled by a pair of numerically-controlled stepper motors was used to move the substrate in the x and y directions. The step size for the scanning was 1 µm and the scanning rate could be adjusted between 1 and 30 mm/min by changing the delay time between steps. The z direction was also controlled by a third stepper motor which fixed the distance between the microplasma system and third electrode. Figure 4.8 shows SEM images of a microfabricated mask and the corresponding patterns of Ag transferred at two different scan rates. The size of the transferred pattern was

**Figure 4.7.** SEM images of AgNO₃/PVA films after exposure to extracted discharge with alumina membrane template at following conditions: (a) 10 minutes and 1000 µA, (b) 30 minutes and 1000 µA, and (c) 30 minutes and 200 µA.

**Figure 4.8** SEM images of (a) stencil mask with 15 µm hole array and Ag patterns transferred at (b) 30 mm/min, and (c) 6 mm/min scan rate. The extracted discharge current was 200 mA, and the primary microplasma current was 4 mA. All scale bars are 100 µm.
found to increase with decreasing scan rate most probably due to increased exposure time (i.e. dwell time) which allows the discharge (electrons) to interact and react with the film longer (i.e. penetrate deeper into the film or diffuse over a larger area). To explore this issue, we also exposed films directly to the extracted discharge (no mask). Figure 4.9 shows photos of films exposed directly to the extracted discharge as a function of scan rate. Higher scan rates are found to produce smaller line widths, confirming that lower exposure times reduce the diffusion of the discharge.
4.4 Summary

In summary, we have studied the formation of an extracted discharge at atmospheric pressure. The generation of a low-current, weakly ionized discharge facilitates nanopatterning applications such as the masked reduction of Ag\(^+\) to metallic Ag. Direct interaction of the “soft” polymeric samples with the plasma is avoided and compared to direct writing, we have reduced the dimension of the transferred patterns by approximately 3 orders of magnitude (100 µm vs. 100 nm). Further reductions in the size of the transferred pattern may be possible with masks fabricated by e-beam lithography.
CHAPTER 5
DIRECTED ASSEMBLY OF METAL NANOPARTICLES USING METALLOPOLYMER FILMS AS MOLECULAR TEMPLATES

5.1 Introduction

In Chapter 4, we demonstrated the formation of an extracted discharge for nanopatterning applications. Patterns were transferred by using lithographic masks which are typically created by chemical or vacuum techniques (e.g. electron beam). An alternative approach to patterning nanomaterials is self- or directed-assembly. This is achieved by the physiochemical properties of a material which result in organization of superstructures through interatomic forces (e.g. van der Waals, charge, etc) and external stimuli. Previously, block copolymer molecules have been self-assembled to create templates for nanopatterning [27, 28, 29]. In this chapter, we introduce a similar but fundamentally new direction for directed assembly of nanomaterials: we use metallo-supramolecular polymers (metallopolymer) which contain both polymer and inorganic (metal) components to produce unagglomerated, assembled films of metal nanoparticles [100, 101, 102]. Previously, metallopolymer films have been shown to exhibit lamellar morphology as a result of their unique multiphase properties [103]. The lamellar period is on the order of 10 nm [30], a length scale that is comparable to the capabilities of electron beam lithography. By exposing the metallopolymer template to a plasma, the metal moieties are reduced to nucleate metal clusters and produce a patterned film of metal nanoparticles. Overall, this approach to nanopatterning has the potential to
overcome current limitations associated with lithography and is amenable to low cost, large scale production of patterned, hybrid metal/polymer structures.
5.2 Experimental details

Materials: All reagents and solvents were purchased from Aldrich and used without further purification. Spectrophotometric grade chloroform was used for all experiments. Macromonomers 1, 2, and 3 were synthesized as previously reported [104, 105]. 

Pt(DMSO)$_2$Cl$_2$ was prepared according to the literature [106]. Molecular weights ($M_n$) for 1, 2, and 3 were 4200, 9600, and 4000 g/mol respectively.

Extracted discharge: Details of the experimental setup used to operate the extracted discharge are provided in Chapter 4.3. Briefly, a microplasma was ignited between a stainless-steel capillary tube (Restek, Inc., I.D. = 180 lm, L = 5 cm) and a metal grid anode. An extracted discharge was formed by biasing a third electrode or substrate with a positive high voltage. All polymer film exposures were performed with the microplasma discharge operated at 150 sccm Ar and 4 mA. The substrate was positioned 0.5 cm downstream of the anode of the microplasma.

Instruments: Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 600 NMR spectrometer. Small-angle X-ray scattering (SAXS) measurements were conducted using a Rigaku S-MAX 3000 SAXS system. Cu Kα X-rays from a MicroMax-002+ sealed tube source ($λ$ = 0.154 nm) were collimated through three pinhole slits to yield a final spot size of 0.7 mm at the sample position. The sample-to-detector distance and the scattering vector, $q$, were calibrated using a silver behenate (AgBe) standard with a characteristic (001) peak position at $q = 1.076$ nm$^{-1}$. The calculated sample-to-detector distance was 1.5 m. Typical exposure times were 1 h. Wide-angle X-ray scattering
(WAXS) measurements were conducted using a Rigaku SA-HF3 X-ray generator and D/MAX2000/PC series diffractometer. Differential scanning calorimetry (DSC) experiments were performed on a TA Instruments Q200 DSC equipped with a refrigerated cooling system. All samples were run under a flowing nitrogen purge and were heated and cooled at a rate of 10 °C/min. Dynamic mechanical thermal analysis experiments were performed using a TA Instruments DMA Q800 under N2 with liquid N2 cooling and heated at a rate of 10 °C min⁻¹. The UV lamp used for reduction experiments was a Bluepoint 4 Ecocure from Honle UV America, Inc. All experiments were carried out with a 320 – 500 nm filter. High resolution transmission electron microscopy (HRTEM) was performed with a Philips Tecnai F30 operated at 300 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI VersaProve XPS Microprobe. A monochromatic AlKα (1486.6 eV) source was used with a spot size of 300 µm.

**Synthesis of [Pt₂(1-3)Cl₂](Cl₂):** A solution of 1 (250 mg, 0.06 mmoles) in chloroform (40 mL) was added to a suspension of Pt(DMSO)₂Cl₂ (50.3 mg, 0.12 mmoles) in methanol (10 mL) under inert atmosphere. Complexation was carried out at 50 °C for 24 h. After removal of the solvent, the resulting orange solid was washed multiple times with water and ether to give the desired product in quantitative yield. δH (600 MHz; CDCl₃) 7.51 (d, 4H, Ar), 7.23 (t, 4H, Ar), 7.13 (t, 4H, Ar), 7.03 (s, 4H, Ar), 6.97 (d, 4H, Ar), 4.42 (t, 4H, -OCH₂⁻), 3.76 (s, 12H, -NCH₃), 3.40, (m, 256H, -OCH₂CH₂⁻), 1.61 (m, 260H, -OCH₂CH₂⁻) δC (100 MHz; CDCl₃) 152.2, 147.8, 137.5, 133.5, 126.2, 125.3, 115.2, 112.0, 110.6, 70.6, 32.4, 26.2. The same conditions were used for 2 with values of: 2 (50 mg,
0.005 mmoles) and Pt(DMSO)$_2$Cl$_2$ (4.4 mg, 0.01 mmoles). The same conditions were used for 3 with values of: 3 (200 mg, 0.05 mmoles) and Pt(DMSO)$_2$Cl$_2$ (42.2 mg, 0.1 mmoles). $\delta_H$ (600 MHz; CDCl$_3$) 7.50 (d, 4H, Ar), 7.23 (t, 4H, Ar), 7.13 (t, 4H, Ar), 7.04 (s, 4H, Ar), 6.99 (d, 4H, Ar), 4.42 (t, 4H, -OCH$_2$-), 3.77 (s, 12H, -NCH$_3$), 1.48-0.94 (m, 398H, -CH$_2$-; -CH-), 0.94-0.79 (m, 125H, -CHCH$_3$-) $\delta_C$ (100 MHz; CDCl$_3$) 152.2, 147.8, 137.5, 133.5, 126.2, 125.3, 115.2, 112.0, 110.6, 68.7, 39.0, 37.8, 33.4, 32.5, 30.3, 26.7-25.6, 10.9-10.2.

**Preparing thin films of metallopolymers for plasma electrochemical reduction:** 0.5 mM solutions of [Pt$_2$(1-3)Cl$_2$](Cl$_2$) in CHCl$_3$ were used to create all films unless otherwise stated. To avoid the possibility of photo-reduction from ambient light exposure, the solutions and subsequent films were covered with aluminum foil. Thin films were prepared by spin-coating onto a carbon-coated TEM grid (Electron Microscopy Sciences) at 2000 rpm for 60 s. The films were vacuum dried at 40 °C overnight. In between experiments, the films were placed in a desiccator and stored -10 °C - this was found to be essential to avoid degradation of the metallopolymer. Films were exposed to the extracted discharge for a variety of times (30, 60, and 180 mins) at fixed conditions.

**Preparing thick films of metallopolymers for structural characterization:** Thick films were prepared by simple casting of solutions of metallopolymers. 200 mg of [Pt$_2$(1)Cl$_2$](Cl$_2$) or [Pt$_2$(3)Cl$_2$](Cl$_2$) were dissolved in 2 mL of CHCl$_3$ and cast into an aluminum walled casting dish with a Teflon sheet bottom. The solvent was allowed to
evaporate at room temperature for 24 h followed by vacuum drying at 40 °C overnight to yield mechanically stable films with thicknesses of 180 ± 30 μm.
5.3 Results and discussion

The Pt metallopolymers ([Pt\(_2\)(1-3)Cl\(_2\)](Cl\(_2\))) was synthesized by reacting macromonomers 1-3 with Pt(DMSO)\(_2\)Cl\(_2\) at 50 °C overnight as shown in Figure 5.1a. This metallopolymers is characteristic of a well-ordered morphology because of the combination of weak Pt – Pt interactions with phase separation. Thus, exposure to an extracted discharge should result in the formation of a directly assembled pattern of Pt nanoparticles [see Figure 5.1b].

To evaluate the ability of Pt metallopolymers to serve as a molecular template for directed assembly of metal nanoparticles, the morphology was studied using SAXS and WAXS. The SAXS of films of [Pt\(_2\)(1)Cl\(_2\)](Cl\(_2\)) and [Pt\(_2\)(3)Cl\(_2\)](Cl\(_2\)) both show scattering

![Diagram](image)

**Figure 5.1.** (a) Synthesis of the platinum metallo-supramolecular polymers [Pt\(_2\)(1-3)Cl\(_2\)](Cl\(_2\)). (b) Schematic of platinum nanoparticle formation from the reduction of [Pt\(_2\)(1-3)Cl\(_2\)](Cl\(_2\)) via plasma electrochemistry.
which is consistent with a lamellar-like morphology as a result of phase separation between the metal-ligand complexes and the polymer cores. For films prepared with [Pt$_2$(3)Cl(CH$_2$)$_2$]Cl$_2$, two strong scattering peaks are observed with a primary Bragg diffraction peak ($q^*$) at $q = 0.72$ nm$^{-1}$ and a secondary scattering peak ($2q^*$) at half the distance of the primary peak as shown in Figure 5.2a. This type of scattering is indicative of a lamellar morphology with alternating domains of the metal-ligand complex and polymer core as a result of phase separation. In this case, the metal-ligand complexes act as a “hard” phase and the low $T_g$ polymer core (ca. -80 °C for 1 and 2 and ca. -40 °C for 3) acts as the “soft” phase which is consistent with previous results seen with other metallo-

![Figure 5.2](image)

**Figure 5.2.** Morphological characterization of metallo-supramolecular polymers [Pt$_3$(1)Cl(CH$_2$)$_2$][Cl$_2$] and [Pt$_2$(3)Cl(CH$_2$)$_2$][Cl$_2$]. Films of [Pt$_3$(3)Cl(CH$_2$)$_2$][Cl$_2$] display strong scattering peaks consistent with a lamellar morphology by (a) small angle X-ray scattering (SAXS) and (b) wide angle X-ray scattering (WAXS) shows only one short Pt – Pt distance within the metal-ligand phase. (c) [Pt$_3$(1)Cl(CH$_2$)$_2$][Cl$_2$] films also show lamella in the SAXS but with reduced long-range order. (d) WAXS of [Pt$_3$(1)Cl(CH$_2$)$_2$][Cl$_2$] display both “long” and “short” Pt – Pt distances in the metal-ligand hard phase.
supramolecular films. The lamellar period, \(d\), which is given as \(d = 2\pi/q^*\) is approximately 8.6 nm which correlates to the lamellar spacing between the metal-ligand “hard” phases.

The WAXS diffractogram for \([\text{Pt}_2(3)\text{Cl}_2](\text{Cl}_2)\), Figure 5.2b, displays one dominant scattering peak at \(2\theta = 26.3^\circ\) \((d = 3.39 \, \text{Å})\) as well as broad peaks at \(2\theta = 19.2^\circ\) and \(12.1^\circ\) \((d = 4.67\) and \(7.31 \, \text{Å}\) respectively) which result from the amorphous polymer core. The peak at 3.39 Å relates to the structure of the metal-ligand “hard” phase, specifically the Pt - Pt distance, where the Pt\(^{2+}\) ions are evenly spaced within the hard phase. This value matches closely to those previously reported for vapochromic Pt\(^{2+}\):Mebip complexes which had been exposed to solvent vapor to produce a red color [107]. Both the Pt – Pt distance \((d = 3.39 \, \text{Å})\) and color (dark orange/red) for films of \([\text{Pt}_2(3)\text{Cl}_2](\text{Cl}_2)\) are consistent with strong Pt – Pt interactions within the metal-ligand phase. As there should be no residual solvent in these films, these results suggest that the phase separation between the nonpolar polymer core and ionic metal-ligand complexes is primarily responsible for the short, repeatable Pt – Pt distance observed in the WAXS results.

In a similar manner, the SAXS of films of \([\text{Pt}_2(1)\text{Cl}_2](\text{Cl}_2)\), Figure 5.2c, show two peaks with a primary diffraction peak \((q^*)\) at \(q = 0.75\) \(\text{nm}^{-1}\) \((d = 8.4\) nm) and a secondary peak \((2q^*)\) at \(q = 1.53\) \(\text{nm}^{-1}\) \((d = 4.1\) nm) characteristic of a lamellar structure, however the relative intensity of the scattering peaks is much weaker than those seen for the \([\text{Pt}_2(3)\text{Cl}_2](\text{Cl}_2)\) film. The decreased scattering intensity implies that the long-range ordering of the lamellae is inferior than that seen in the \([\text{Pt}_2(3)\text{Cl}_2](\text{Cl}_2)\) films. The decreased intensity in the SAXS for \([\text{Pt}_2(1)\text{Cl}_2](\text{Cl}_2)\) films is likely a result of poor phase separation between the metal-ligand complexes and the polymer core arising from the
presence of oxygen atoms along the polymer backbone. The increased polarity of the poly(tetrahydrofuran) core of [Pt₂(1)Cl₂](Cl₂) along with the potential for the polymeric oxygen atoms to weakly coordinate with the Pt²⁺ ions of the metal-ligand complexes are believed to be responsible for the observed decrease in phase separation when compared to films prepared with [Pt₂(3)Cl₂](Cl₂).

The WAXS pattern for the [Pt₂(1)Cl₂](Cl₂) film also shows multiple scattering peaks rather than the one dominant peak seen in the [Pt₂(3)Cl₂](Cl₂) film [See Figure 5.2d]. The peaks in the film of [Pt₂(1)Cl₂](Cl₂) correspond to distances of 16.19, 7.97, 5.71, 3.78, and 3.38 Å. The shortest distances match closely with previously reported lengths corresponding to alternating long and short Pt – Pt distances (5.71 and 3.38 Å respectively) and interplaner distances between the Mebip ligands (3.78 Å) which is suggestive of a connected dimer-type motif [108]. The larger distance peaks are not a result of crystallization in the polymer core as heating the sample above the melting temperature (Tₘ) did not affect the peaks [See Figure 5.3]. Rather, the peaks

![Figure 5.3. WAXS of [Pt₂(1)Cl₂](Cl₂) before and after annealing demonstrating that the observed peaks are not a result of crystallization of the polymer core.](image)
corresponding to the larger distances are thought to be a result of longer Pt – Pt interactions; however their origin is unknown at this point. The presence of long and short Pt – Pt interactions (d = 5.71 and 3.38 Å) also helps explain the color of the film being more orange for films of [Pt$_2$(1)Cl$_2$](Cl$_2$) unlike the dark orange/red [Pt$_2$(3)Cl$_2$](Cl$_2$) film which shows only one short Pt – Pt distance.

To nucleate metal nanoparticles, thin films of [Pt$_2$(I-3)Cl$_2$](Cl$_2$) were prepared by spin-coating onto a substrate and then exposed to extracted electrons using the set-up shown in Figure 4.1. Figure 5.4 shows TEM images of films of [Pt$_2$(1)Cl$_2$](Cl$_2$) after exposure to the extracted discharge for various times. As-deposited films which were not exposed to the extracted discharge showed no discernible features [Figure 5.4a]; after 30

![Figure 5.4](image_url) **Figure 5.4.** TEM images of [Pt$_2$(1)Cl$_2$](Cl$_2$) for the various exposed time of extracted discharge. (a) unexposed and (b) 0.5 hr., (c) 1 hr., (d) 3 hrs. Inset shows high resolution TEM displaying typical platinum crystalline lattice spacing. Extracted discharge was operated with 200 µA current.
minutes of exposure, nanoparticles could be clearly observed [Figure 5.4b]. Longer exposure resulted in an increase in the average particle size as shown in Figure 5.4c and 5.4d for exposure times of 1 hour and 3 hours, respectively. TEM analysis reveals that the Pt nanoparticles are unagglomerated, spherical, and crystalline with highly uniform size distributions. Similar results were obtained for films prepared from [Pt$_2$(2)Cl$_2$](Cl$_2$) [Figures 5.5] and [Pt$_2$(3)Cl$_2$](Cl$_2$) [Figure 5.6]. We note that the nanoparticles form well-dispersed arrays and appear to form patterns that follow the polymer lamellae in all cases.

**Figure 5.5.** TEM images of [Pt$_2$(2)Cl$_2$](Cl$_2$) (0.5 mM) (a) unexposed and exposed to extracted discharge for (b) 0.5 hr., (c) 1 hr., and (d) 3 hrs. Extracted discharge current is 200 µA.
We confirmed the material phase and crystallinity of the nucleated nanoparticles using TEM. The inset in Figure 5.6d shows that the measured lattice spacing corresponds well to the Pt(111) and Pt(200) crystalline planes of the fcc (face centered cubic) crystalline phase of bulk Pt (JCPDS file 87-0644). Furthermore, XPS was used to examine the change in valence states of Pt before and after discharge exposure. XPS spectra were obtained for films of [Pt$_2$(1)Cl](Cl$_2$) drop cast on a Si substrate and exposed to the extracted discharge for 3 hours. As shown in Figure 5.7, XPS spectra for the initial (unexposed) film show no peaks while the exposed film shows peaks at 74.4 eV and 71.2 eV which can be assigned to Pt 4f5/2 [109] and Pt 4f7/2 [110], respectively. These binding energies are slightly shifted from that of Pt$^0$, most probably due to charging of

**Figure 5.6.** TEM images of [Pt$_2$(3)Cl$_2$](Cl$_2$) (0.5 mM) (a) as-deposited and after exposure to extracted discharge for (b) 0.5 hr, (c) 1 hr, and (d) 3 hrs.
the polymer [111]. To eliminate charging, we sputtered the sample to remove the polymer coating and compared the peaks with bulk Pt foil (ESPI, Inc). As shown in Figure 5.8, after sputtering, the XPS spectra confirmed the presence of metallic Pt in the reduced metallopolymer film.

**Figure 5.7** XPS spectra of Pt metallopolymer film before and after exposure to extracted discharge. (a) Survey spectra and (b) high-resolution spectra of Pt 4f region. Samples were prepared by drop casting a solution of [Pt2(1)Cl2](Cl2) on a Si substrate and exposing to extracted discharge for 3 hours.

**Figure 5.8.** XPS spectra of Pt metallopolymer films exposed to extracted discharge and sputtered for indicated times. (a) Survey spectra and (b) high-resolution spectra of Pt 4f region. Samples were prepared by drop casting a solution of [Pt2(1)Cl2](Cl2) on Cu foil and exposing to extracted discharge for 3 hours.
Although nanoparticles were successfully formed by exposure to extracted discharge, it is not clear if the electrons in the extracted discharge are responsible for reduction of the Pt moieties in the metallopolymer film. Previous reports have demonstrated the reduction of metal ions by other methods including electron beams [85, 84, 85], heating [88, 89, 90], UV irradiation [82, 82, 87], and chemical [112, 113, 114]. To explore whether heating or UV light could be responsible for the reduction of the metallopolymer, we carried out a control experiment by exposing a film to a current of 0 µA – this ensured that no electrons would interact with the film while heating and UV light are still present from the main microplasma discharge. As shown at Figure 5.9, the sample exposed to zero current in the extracted discharge showed no nanoparticles while our standard exposure (200 µA) resulted in nanoparticle formation. We also attempted to reduce the metallopolymer by irradiating with an intense UV light source characterized by 320-500 nm radiation and a surface intensity of 100 mW/cm² for three hours. Again, no nanoparticles were observed by TEM [Figure 5.9c]. Chemical reduction was studied by refluxing [Pt₂(1)Cl₂](Cl₂) in ethylene glycol using an adapted procedure reported by Urbina and coworkers on the reduction of platinum nitrate. After refluxing [Pt₂(1)Cl₂](Cl₂) in ethylene glycol for three hours, the ethylene glycol was removed, the product was redissolved in chloroform, and spin-coated onto a TEM grid. Once again no nanoparticle formation could be observed as shown in Figure 5.9d. We also looked at the potential reduction by the TEM itself as TEM uses an electron beam for imaging. A [Pt₂(1)Cl](Cl₂) film was spin-coated onto a TEM grid and exposed to 300 kV. Images in Figure 5.10 show that up to 10 minutes exposure, the [Pt₂(1)Cl](Cl₂) film is very stable and no particle formation was observed. In addition, any further growth of Pt
Figure 5.9. TEM images on the potential for platinum reduction by common reduction techniques. (a) 1 hr exposure to extracted discharge (M:4 mA, ED:200 mA) (b) 1 hr exposure with microplasma (M:4 mA, ED:0 mA) (c) UV exposure (320-500 nm, 100 mW/cm², 3 hrs.) (d) Refluxed in ethylene glycol (150 °C, 3 hrs.)

Figure 5.10. TEM images of an unexposed [Pt₂(1)Cl₂](Cl₂) film under the TEM’s electron beam for (a) 0 min., (b) 3 mins., and (c) 10 mins. demonstrating that no particles are formed.
nanoparticles which were already formed using an extracted discharge by the e-beam of the TEM was monitored [see Figure 5.11]. The size of Pt nanoparticles that were continuously monitored were not found to increase. Based on these experiments, we conclude that the formation of Pt nanoparticles from a metallopolymer film requires exposure to a plasma discharge and the mechanism for reduction and particle nucleation is reaction with electrons (i.e. electrochemical).

We systemically investigated the effect of polymer morphology on nanoparticle formation by comparing the reduction of $[\text{Pt}_2(1)\text{Cl}_2](\text{Cl}_2)$ vs $[\text{Pt}_2(3)\text{Cl}_2](\text{Cl}_2)$ and metal loading ($[\text{Pt}_2(1)\text{Cl}_2](\text{Cl}_2)$ vs $[\text{Pt}_2(2)\text{Cl}_2](\text{Cl}_2)$). Overall, the lamellar structure of the nanoparticles are controlled by the polymer morphology and metal loading [see Figure 5.12]. For films prepared from $[\text{Pt}_2(3)\text{Cl}_2](\text{Cl}_2)$, we found smaller nanoparticles and shorter center-to-centers distance as compared to $[\text{Pt}_2(1)\text{Cl}_2](\text{Cl}_2)$ [see Figures 5.13(a) and (c)]. For a given polymer, increasing the Pt loading was found to decrease the particle size and center-to-center distance.

To better understand the mechanism for particle formation in the various polymer films, we plotted the particle size and density as a function of exposure time. The particle size and density were calculated with the TEM images which were obtained at three different area of the sample and repeated two times. Figure 5.13a shows that in all cases the particle size increases rapidly at initial times then reaches a maximum value. Interestingly, we find a clear trend in average size and density for the different polymer films. Pt nanoparticles created from $[\text{Pt}_2(1)\text{Cl}_2](\text{Cl}_2)$ have the largest average diameter, followed by $[\text{Pt}_2(2)\text{Cl}_2](\text{Cl}_2)$, and finally films prepared with $[\text{Pt}_2(3)\text{Cl}_2](\text{Cl}_2)$ generated the smallest particles. The trend of particle density was found to be opposite to that of
Figure 5.12 TEM images of (a) [Pt$_2$(1)Cl$_2$](Cl$_2$) (0.5 mM), (b) [Pt$_2$(2)Cl$_2$](Cl$_2$) (0.5 mM) (c) [Pt$_2$(3)Cl$_2$](Cl$_2$). Extracted discharge was exposed for 30 minutes with 200 µA.

Figure 5.11. TEM images of Pt nanoparticles formed from [Pt$_2$(1)Cl$_2$](Cl$_2$) (extracted electron current: 200 µA; plasma current: 4 mA; exposure time: 1 hr.; temperature: 0 °C) showing no additional growth in the TEM during imaging for (a) 0 min, (b) 1 min, (c) 3 min, and (d) 5 min.
the particle size, where \([\text{Pt}_2(3)\text{Cl}_2](\text{Cl}_2)\) yields the highest particle density and \([\text{Pt}_2(1)\text{Cl}_2](\text{Cl}_2)\) has the lowest particle density. We believe both of these trends are consistent with nanoparticle formation and growth by means of a chain-end diffusion mechanism in the metallo-supramolecular polymer. In general, nanoparticle formation is initiated when the extracted discharge reduces some of the Pt\(^{2+}\):Mebip complexes and nucleates Pt\(^0\). These nucleated clusters then grow in size as the Pt\(^{2+}\):Mebip chain-ends diffuse and deposit additional Pt. The final Pt particle size and density are determined by the structural characteristics of the metallo-supramolecular polymers. Films of \([\text{Pt}_2(3)\text{Cl}_2](\text{Cl}_2)\) formed the smallest diameter particles and highest particle density, and if we assume a chain-end diffusion mechanism, the diffusion should be primarily limited to within the metal-ligand phase because of the strongly phase separated morphology. The nonpolar core of the \([\text{Pt}_2(3)\text{Cl}_2](\text{Cl}_2)\) films will also greatly hinder diffusion of the ionic, metal-ligand complexes through the polymer such that diffusion from one metal-ligand

![Figure 5.13](image.png)

**Figure 5.13.** (a) Particle size and (b) density of Pt nanoparticles in various metallo-polymer films as a function of extracted discharge exposure time. The extracted discharge was operated at 200 \(\mu\)A in all cases. Particles were analyzed over a 30 nm x 30 nm square area.
phase to another should be severely hampered. Similarly, films prepared from \([\text{Pt}_2(1)\text{Cl}_2](\text{Cl}_2)\) yield larger nanoparticles and lower particle densities as the polarity of the polyether core should allow for better diffusion of the chain-ends between metal-ligand phases. The lamellar ordering in the \([\text{Pt}_2(1)\text{Cl}_2](\text{Cl}_2)\) film was also greatly diminished as a result of decreased phase separation. The decreased phase separation should also increase the ability of the metal-ligand chain-ends to diffuse from one “hard” phase to another.

We explored the effect of the \(\text{Pt}^{2+}\).Mebip end-groups on particle nucleation and growth by varying the molecular weight of the polymer core between the metal-ligand phases. The molecular weight of macromonomer 2 is roughly two times that of 1 (9600 g/mol vs 4200 g/mol respectively) which allows us to change the polymer core by a considerable amount. Our results show that although they share the same polymer core, films of \([\text{Pt}_2(1)\text{Cl}_2](\text{Cl}_2)\) produce larger nanoparticles and a smaller density than \([\text{Pt}_2(2)\text{Cl}_2](\text{Cl}_2)\). Nanoparticles grown from the film prepared at higher precursor concentration yield smaller particles with a higher particle density which is consistent with an increase in nucleation points as the concentration of end-groups is increased. Thus, using metallo-supramolecular polymers as templates, nanoparticles of different sizes can be created by varying the extracted discharge exposure time, changing the core polymer, or the concentration from which the films are prepared.

We finally would like to address why the particle number density initially increases with exposure time, then reaches a maximum and eventually decreases with exposure time. As previously pointed out, particle nucleation and growth should depend on several factors including the metal concentration, diffusion of metal atoms, etc. The particle density could decrease at longer times because the particles grow by coalescence,
i.e. smaller particles combine to form larger particles. However, the particle density could also decrease if particles are somehow “lost” – this could be an artifact of our measurement if particles diffuse from the surface into the bulk of the film where they cannot be observed by TEM. We estimated the total volume of Pt in the TEM images by assuming the Pt particles to be perfect spheres with an average radius, $r$:

$$\text{Total volume (Pt NPs)} = \text{Single particle volume} \times \text{# of particles \ (at 900 nm}^2)$$

$$= \frac{4}{3} \pi r^3 \times \text{# of particles}$$

Our calculations show that the total volume of Pt does not decrease with exposure time for all the films ([Pt$_2$(1)Cl$_2$](Cl$_2$): (64.7 $\rightarrow$ 665.5); [Pt$_2$(2)Cl$_2$](Cl$_2$): (149.6 $\rightarrow$ 460.5); [Pt$_2$(3)Cl$_2$](Cl$_2$): (108 $\rightarrow$ 220.7); the unit is nm$^3$ / 900nm$^2$ and the change from 0.5hr to 3hr exposure). Based on this analysis, our picture of particle nucleation and growth is the following: initially, plasma exposure results in nucleation of particles. At longer exposure times, particle nucleation slows and the particles grow by deposition of new precursor on the existing particles. Eventually, particle nucleation stops, but particles continue to grow by coalescence. This picture is consistent with an initial increase in particle size and density, followed by a decrease in particle density at longer times [see Figure 5.13].
5.4 Summary

In this chapter, we have demonstrated a new approach to directly assemble films of patterned metal nanoparticles from molecular metallopolymer templates. Uniform, unagglomerated Pt nanoparticles are formed with diameters less than 5 nm. The nanoparticle size and density in the films were found to be influenced by the polymer core of the macromonomer with polar, poly(tetrahydrofuran) cores giving the largest particle size while nonpolar, poly(ethylene-co-butylene) cores yielded the smallest particle sizes as a result of the degree of phase separation in the metallo-supramolecular polymer films. The combination of metallopolymer chemistry and plasma reduction is attractive for roll-to-roll processing applications whereby novel flexible, patterned films of metal nanoparticles are produced at low cost and large scales.
CHAPTER 6
CHEMICALLY REACTIVE HYDROGEN PLASMAS FOR REDUCTION OF
MATERIAL SURFACES: THE EXAMPLE OF GRAPHENE OXIDE

6.1 Introduction

Up to now, we have discussed several examples of plasma electrochemical reduction including the reduction of aqueous ions in solutions (Chapter 2) and reduction of metal ions dispersed with polymers as thin films (Chapter 3 and 4) and reduction of novel metallopolymer precursors (Chapter 5). The concept of plasma electrochemistry is unique because an inert plasma discharge is used to activate reactions using only the electrons in the plasma discharge. A more conventional approach to activating reactions is a chemically reactive plasma whereby radical species such as atomic hydrogen are generated. The reduction of certain materials such as graphene oxide (GO) requires such reaction chemistry in order to remove relatively stable oxygen functional groups [115]. In this chapter, we present a systematic study of hydrogen plasma reduction of graphene oxide. Broadly, these studies show that our plasmas can be used to reduce materials via both electron and chemical activation.

Graphene, because of its unique structure and properties [116,117], has elicited enormous interest for field effect transistors (FETs) [118], transparent conductive films [119, 120], lithium-ion batteries [121], supercapacitors [122], organic photovoltaic cells [123, 124], electron field emitters [125], ultrasensitive sensors [126], and hydrogen storage [127, 128, 129]. So far, several methods have been developed to produce graphene including mechanical cleavage of highly oriented pyrolytic graphite (HOPG)
sublimation of silicon from silicon carbide [131, 132], and thermal [133, 134] or plasma-enhanced [135] chemical vapor deposition (CVD) from a carbon feedstock gas. Graphene oxide (GO) is a promising alternative for bulk production of graphene-based materials as it can be synthesized in large quantities from inexpensive graphite powder [136] and solubilized in a variety of solvents [137]. The preparation of a dispersed form of graphene is attractive for low-cost, solution-phase processing of flexible electronic devices [137].

A critical challenge for technological applications of GO is the presence of oxygen functional groups that must be controllably reduced to precisely tune their electronic and optical properties [138]. GO is typically reduced in solution by strong chemical reducing agents such as hydrazine (N$_2$H$_4$) [139, 140] or sodium borohydride (NaBH$_4$) [141]. However, the treatment of GO with these chemicals is time-consuming and generally ineffective, often requiring additional annealing steps [120, 142]. Additionally, hydrazine (in the form of hydrate [115] or dimethylhydrazine vapor [143]) is a dangerous and environmentally toxic chemical that can introduce impurities in the reduced GO. Alternatively, thermal annealing in Ar, H$_2$, or ultrahigh vacuum (UHV) environments has been found to remove oxygen effectively [138, 144] but the high temperatures that are required limit the range of substrates that can be used. For this reason, novel low-temperature, green approaches to GO reduction have been introduced such as flash reduction [145] and electrochemical reduction [146].

Compared with other chemical techniques, plasma discharges offer a unique advantage because nonequilibrium reactions can be performed at low temperature and high purity [147]. In the case of GO, the generation of atomic hydrogen could enable
effective removal of oxygen functional groups [142]. However, plasmas contain energetic species such as ions that can bombard and sputter or damage such atomically thin materials [148].

Based on our plasma electrochemistry experiments, we have developed an atmospheric-press microplasma process for GO reduction. In contrast to our previous experiments, we introduce H$_2$ gas to generate atomic hydrogen in the microplasma. The plasma is kept remote to avoid direct interactions between energetic states (i.e. ions or electrons) in the plasma and the GO film. Overall, we find that this approach allows effective reduction of GO films at low temperature (<150 °C) which is attractive for flexible conductor applications.
6.2 Experimental details

Synthesis of GO: GO was prepared from natural graphite (Asbury Carbons) by a modified Hummers method reported by Kovtyukhova [149]. Briefly, graphite powder (10 g) was stirred and heated at 80°C in a solution of concentrated H₂SO₄ (30 mL), K₂S₂O₈ (5 g), and P₂O₅ (5 g). The mixture was thermally isolated for 6 hours and allowed to cool to room temperature. The preoxidized graphite was then carefully diluted with distilled water, filtered, and washed on the filter until the rinse water pH became neutral. The product was dried in air at ambient temperature overnight. This preoxidized graphite was then subjected to oxidation by Hummers method. The oxidized graphite powder (10 g) was placed in cold (0 °C) concentrated H₂SO₄ (230 mL). KMnO₄ (30 g) was added gradually with stirring and cooling, so that the temperature of the mixture was not allowed to reach 20°C. The mixture was then stirred at 35 °C for 2 hours followed by the addition of distilled water (460 mL). After 15 minutes, the reaction was terminated by the addition of a large amount of distilled water (1.4 L) and 30 % H₂O₂ solution (25 mL). The mixture was filtered and washed with 1:10 HCl solution (2.5 L) in order to remove metal ions. The GO product was finally suspended in distilled water (1L).

Experimental setup: The remote, atmospheric-pressure microplasma and a tube furnace (Thermolyne 79300) was used to reduce films of GO. Gas flow was coupled to the microplasma by high-pressure gas fittings; all flow rates were controlled by digital mass flow controllers. The microplasma was operated with a DC power supply (Keithley, model 246) between a negatively biased stainless-steel capillary tube (I.D. = 180 μm, L = 5 cm, Restek) and a grounded stainless-steel mesh (Figure 6.1b), separated by 2 mm. To
ignite the plasma, we applied a high voltage (~2 kV). After gas breakdown, the discharge current was controlled by an inline resistor (160 kΩ) on the high voltage side.

**X-ray photoelectron spectroscopy (XPS) characterization of GO films:** XPS characterization of GO films was performed before and after thermal and plasma treatment at a series of temperatures. Carbon 1s core level spectra, oxygen 1s core level spectra, and survey spectra were obtained by a PHI Versa Prove XPS Microprobe equipped with a monochromatic Al Kα (1486.6 eV) source.

**Micro Raman characterization of GO films:** Raman spectroscopy was performed at room temperature using a Jobin-Yvon Horiba LabRam system with a He-Ne laser at an excitation frequency of 633 nm. To obtain spectra, a 17 mW laser beam with a 1 µm spot size was employed. Typical exposure times to collect Raman spectra were 2 min. To confirm that the laser did not cause reduction or other structural changes to the GO samples, we obtained a series of Raman spectra after continuous exposure to the same spot (up to 30 minutes).

**Optical emission spectroscopy (OES):** Excited species generated in the plasma including atomic hydrogen were detected by OES (Ocean Optics HR 4000). The light was collected from the plasma with a fiber optic cable. Spectra were integrated 10 times with an exposure time of 300 ms per scan to obtain a high signal-to-noise.
Sheet resistance measurement: Sheet resistance measurements were performed with a home-made two probe measurement and a constant pressure of 500 psi. The measured resistance ($R$) value was converted to sheet resistance ($R_s$) by the following equation:

$$R = \rho \frac{L}{A} = \rho \frac{L}{W t} = \frac{\rho L}{t W} = R_s \frac{L}{W}$$

$$R_s = \frac{W}{L}$$

where $\rho$ is the resistivity, $A$ is the cross-sectional area, and $L$ is the gap between two electrodes. The cross-sectional area was estimated from the width ($W$) and the thickness ($t$) of the measured sample.

Hydrogenation of graphene: To assess whether hydrogenation of sp$^2$ domains in the GO film could occur during the plasma reduction process (which would be undesirable), we designed a test experiment. High quality graphene films prepared by chemical vapor deposition on Cu foil [150, 151, 152] then transferred onto 300 nm SiO$_2$ on Si substrates by spin-coating polymethylmethacrylate (PMMA) and dissolving the Cu foil in FeCl$_3$ [153, 154, 155] were exposed to atomic hydrogen under the same conditions as the GO films (Ar/H$_2$=50/50, discharge current=10 mA, substrate temperature=150 °C, exposure time = 30 minutes).
6.3 Results and discussion

Figure 6.1a schematically illustrates the experimental setup. GO films were prepared by drop casting an aqueous suspension of GO flakes on Au foil (25 μm, ESPI) or Au-coated Si (300 nm, Sigma Aldrich). Before each experiment, the GO film was loaded into the quartz tube reactor and placed 1.5 cm downstream from the grounded stainless-steel mesh in the afterglow, where charged species in the plasma cannot interact.

![Diagram](image)

**Figure 6.1.** (a) Schematic diagram of experimental setup used for remote, atmospheric-pressure plasma-assisted reduction of GO thin films. A DC microplasma housed inside a quartz tube is formed between a negatively biased stainless-steel capillary tube and a grounded stainless-steel mesh electrode. Gas mixtures of Ar and H₂ are introduced into the microplasma to generate atomic hydrogen (H•). Thin films of GO were drop cast on substrates and placed 1.5 cm from the microplasma to avoid ion and electron bombardment. (b) Photograph of remote microplasma, operated in Ar/H₂ (50/50) at a discharge current of 10 mA and GO film (inset: close-up of microplasma). (c) Photographs of GO films deposited on PET substrates before reduction (left panel) and after thermal treatment at 150 °C (middle panel) or plasma treatment at 150 °C (right panel). All treatments were performed in an Ar/H₂ atmosphere (50/50) at 1 atm (inset: flexibility of GO films after plasma-assisted reduction is demonstrated).
with the film [31]. The reactor was then repeatedly evacuated by an oil-free, dry pump (Welch Vacuum, model 2562B-01) and purged to remove air and water before being brought up to atmospheric pressure with the desired gas flow; atmospheric pressure was maintained during the experiments by exhausting the gas from the reactor without active pumping. The GO films were then treated for 30 min by heating alone or with heating and the plasma operating at a constant discharge current. At the end of each experiment, the plasma and/or heating were shut off, and the furnace was cooled with a gas flow of Ar. Figure 6.1c shows representative photos of GO films on PET before treatment (left panel) and after either thermal annealing (middle panel) or plasma exposure (right panel). It is readily apparent that the plasma treatment results in a darker film. The inset of Figure 6.1c confirms that the GO films reduced on PET remain flexible after plasma treatment.

We designed experiments to decouple the role of atomic hydrogen. The reduction of GO was carried out by the following methods of treatment (i) thermal annealing alone (in an Ar/H\textsubscript{2} atmosphere), (ii) remote Ar plasma with thermal annealing, and (iii) remote Ar/H\textsubscript{2} plasma with thermal annealing. All treatments were performed at atmospheric pressure, and we focused on low temperatures, which are suitable for flexible conductor applications.

We note that even without any heating by the furnace, the plasma itself was found to raise the temperature of the substrate through convective heat transfer. To estimate this temperature, a thermometer was placed at the same distance (1.5 cm) as the GO films from the plasma anode. As shown in Figure 6.2, the temperature measurements showed a steady-state value after approximately 10 min. The final steady-state temperature was a
function of discharge current and the gas atmosphere. The temperature was found to depend on several process parameters including discharge current, gas composition, and distance from the discharge. For the specifications used in this study, we measured a temperature of \(\sim 70\) °C; this was then assumed to be the minimum temperature for our study. We believe that lower temperatures could be accessed by our process by increasing the distance of the substrate from the discharge or lowering the discharge current.

To confirm the generation of atomic hydrogen in the plasma, we employed OES. OES is a powerful tool for characterization of excited states present in a plasma environment and is particularly useful for microplasmas because it is noninvasive.

Figure 6.2. Temperature measurement as a function of time caused by the microplasma. Photographs of (a) Ar microplasma and (b) Ar/H\(_2\) plasma (50/50). (c) Temperature as a function of time at a distance of 1.5 cm from the plasma anode (same as substrate in GO experiment).
Figure 6.3 Optical emission spectra of Ar/H$_2$ microplasma as a function of (a) discharge current and (b) H$_2$ composition. Lines corresponding to Ar excited states and atomic hydrogen (H$_\alpha$) are indicated.

Figures 6.3a,b shows spectra obtained from a microplasma formed in a gas mixture of Ar/H$_2$ at various discharge currents. Overall, intense lines corresponding to Ar are observed in the range of 700 to 800 nm. Importantly, we find a peak at 656.3 nm, which corresponds to atomic hydrogen (H$_\alpha$). Of the three possible states of atomic hydrogen known as the Balmer series, the H$_\alpha$ peak is the most abundant species and easiest to observe by OES [156, 157]. The relative intensity of the H$_\alpha$ peak is found to increase with discharge current in accordance with an increase in the plasma density [144]. Increasing the H$_2$ flow rate (relative to Ar) also increases the intensity of this peak.

The oxygen bonding in the GO films after the various forms of treatment was evaluated by XPS. Figures 6.4a,b shows the carbon 1s (C 1s) core-level spectra collected from GO films after thermal annealing and remote atmospheric-pressure microplasma exposure at various temperatures – both types of treatment were performed in identical Ar/H$_2$ atmospheres. The C 1s signal of the initial fully oxidized GO film is also shown.
and consists of different components that can be deconvoluted into \( \text{C}═\text{C/C}–\text{C} \) (284.6 eV), \( \text{C}–\text{O} \) (286.1 eV), \( \text{C}═\text{O} \) (287.5 eV), \( \text{C}(═\text{O})•(\text{OH}) \) (289.2 eV), and \( \pi–\pi^* \) satellite peak (290.6 eV). These assignments are consistent with previous reports of GO [138]. After remote plasma exposure at 70 °C, the peaks corresponding to \( \text{C}–\text{O} \) (286.1 eV), \( \text{C}═\text{O} \) (287.5 eV), and \( \text{C}(═\text{O})•(\text{OH}) \) (289.2 eV) were reduced [See Figure 6.4b]. In comparison, thermal annealing at 70 °C did not show any significant change to the structure of the C 1s band of GO. At 150 °C, both thermal and plasma-assisted reduction resulted in a decrease in the intensity of peaks corresponding to oxygen species, but the latter produced a more significant change, particularly in regards to \( \text{C}═\text{O} \) and \( \text{C}(═\text{O})•(\text{OH}) \).

With increasing temperature, the oxygen species are present in lesser amounts for both types of treatment, consistent with prior reports for thermal annealing of GO [138].

**Figure 6.4.** (a) C 1s high-resolution XPS spectra of GO thin films before and after thermal reduction in an \( \text{Ar/H}_2 \) (50/50) background. (b) C 1s high-resolution XPS spectra of GO thin films before and after \( \text{Ar/H}_2 \) (50/50) plasma-assisted reduction at various temperatures (discharge current = 10 mA). All reduction was performed at atmospheric pressure for 30 min. The spectra were fit by Doniach–Sunjic function after subtracting a Shirley background, as indicated for the spectra at 150 °C. The different components related to various chemical shifts of carbon bonds are indicated.
The atomic percentages of the various carbon bonds in the reduced GO films were determined by analyzing the C 1s XPS spectra at 150 °C (Table 6.1). The majority of oxygen species in the pristine GO film are in the form of C–O bonds. Plasma-assisted reduction was found to more effectively reduce the number of C–O bonds as well as C=O and C(=O)•(OH) species that have been found to decorate the edges of GO sheets and are believed to be more difficult to remove [158].

Table 6.1. Atomic percentages of different carbon bonds identified by XPS in GO thin films reduced by thermal treatment only and plasma-assisted treatment in an Ar/H₂ atmosphere at 150 °C and 1 atm.

<table>
<thead>
<tr>
<th></th>
<th>C=C/C–C</th>
<th>C–O</th>
<th>C=O</th>
<th>C(=O)•(OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal reduction</td>
<td>72</td>
<td>16</td>
<td>6.4</td>
<td>5.6</td>
</tr>
<tr>
<td>Plasma-assisted reduction</td>
<td>83.4</td>
<td>12.7</td>
<td>2.1</td>
<td>1.8</td>
</tr>
</tbody>
</table>

The atomic percentages of the various carbon bonds in the reduced GO films were determined by analyzing the C 1s XPS spectra at 150 °C (Table 6.1). The majority of oxygen species in the pristine GO film are in the form of C–O bonds. Plasma-assisted reduction was found to more effectively reduce the number of C–O bonds as well as C=O and C(=O)•(OH) species that have been found to decorate the edges of GO sheets and are believed to be more difficult to remove [158].

Figure 6.5. XPS survey spectra of GO films after (a) thermal treatment and (b) plasma treatment as a function of temperature. Reduction was performed in a gas atmosphere of Ar/H₂ (50/50) at atmospheric pressure for 30 min in both cases.
The overall oxygen content in the treated GO films was obtained as a function of temperature from XPS survey spectra [see Figure 6.5]. Figures 6.6a,b shows the atomic percentage (C 1s %, O1s %) and atomic ratio (C 1s/O 1s), respectively, after each treatment, and the calculated results are summarized in Table 6.2. The C/O atomic ratio is found to be significantly higher for plasma-reduced GO (6.95) than thermally reduced GO (3.37) at 150 °C; in fact, this value is even higher than GO thermally reduced at 300 °C (6.35). Whereas the oxygen content in the GO films after thermal reduction (22.9%) and Ar plasma-assisted reduction (21.2%) are similar and relatively high, the addition of H₂ to the plasma (12.5%) results in a significant removal of oxygen functional groups. This confirms that atomic hydrogen leads to enhanced reduction of GO at low process temperatures. Moreover, the similar levels of oxygen in GO films after thermal reduction and Ar plasma-assisted reduction confirms that there is no significant ion bombardment in our remote plasma system because low-energy ions are sufficient to remove oxygen [159].

![Figure 6.6](image)

**Figure 6.6.** (a) Atomic percentage of C and O and (b) ratio of C 1s:O 1s XPS signal for thermal-reduced and plasma-reduced GO thin films at various temperatures.
Structural changes to the GO films as a result of plasma exposure were evaluated by micro Raman spectroscopy. Raman spectra were collected at an excitation wavelength of 633 nm and 17 mW power, which was low enough to avoid damage to the samples during measurements [Figure 6.7]. Figure 6.8 shows a series of Raman spectra obtained for GO films treated by thermal reduction alone, Ar plasma-assisted reduction, and Ar/H2 plasma-assisted reduction. The Raman spectrum of the as-deposited GO film reveals a D-band at 1350 cm⁻¹ and a G-band at 1600 cm⁻¹, the latter corresponding to the first-order scattering of the E2g mode [160,161]. The prominent D peak is due to structural imperfections created by oxygen functional groups in the carbon basal plane. After each of the various treatments, no significant changes were observed in the spectra. According to Tuinstra and Koenig [162], the in-plane sp² crystallize size can be estimated

<table>
<thead>
<tr>
<th></th>
<th>C (%)</th>
<th>O (%)</th>
<th>C/O</th>
<th>Sheet resistance (Ω/sq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>66.09</td>
<td>33.91</td>
<td>1.95</td>
<td>∞</td>
</tr>
<tr>
<td>Thermal reduction (150°C)</td>
<td>77.10</td>
<td>22.90</td>
<td>3.37</td>
<td>2.14 × 10⁶</td>
</tr>
<tr>
<td>Ar plasma-assisted reduction (150°C)</td>
<td>78.80</td>
<td>21.20</td>
<td>3.72</td>
<td>-</td>
</tr>
<tr>
<td>Ar/H2 plasma-assisted (150°C)</td>
<td>87.50</td>
<td>12.50</td>
<td>6.95</td>
<td>4.77 × 10⁴</td>
</tr>
<tr>
<td>Thermal (300°C)</td>
<td>86.40</td>
<td>13.60</td>
<td>6.35</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.2. XPS analysis of carbon and oxygen content and C 1s/O 1s (atomic ratios) and sheet resistance in as-prepared GO thin films and reduced GO thin films after various methods of treatment. The temperature was 150 °C and the pressure was 1 atm for all treatments. Thermal treatment was performed in an Ar/H2 atmosphere.
from the ratio of the intensity of the D to G peaks ($I_D/I_G$). Previous reports have shown that reduction by hydrazine hydrate results in a higher $I_D/I_G$ ratio that corresponds to a decrease in the sp2 cluster size perhaps caused by the creation of defects, vacancies, or distortions of the sp2 domains due to the removal of oxygen from the graphene sheets [163, 164]. In our case, the $I_D/I_G$ ratio before and after reduction remains essentially the same [see inset of Figure 6.8], indicating that the plasma treatment does not introduce additional defects into the reduced GO film.

To assess the feasibility of our approach for flexible conductor applications, we measured the sheet resistance of GO films reduced on PET. The thickness of the as-deposited films was $\sim 6 \, \mu$m, and assuming that the reduction occurs only near the surface, the measurement should be independent of film thickness [165]. Raman spectra of the films indicated that the reduction occurred similarly on PET, as in the case of Au
substrates. To obtain sheet resistance, we measured the resistance of the reduced films with a two-point probe and applied the following relationship

\[ R_s = R \frac{W}{L} \]

where \( R \) is the resistance, \( W \) is the width, and \( L \) is the length between two electrodes. As shown in Table 6.2, the sheet resistance after plasma-assisted reduction is \( 4.77 \times 10^4 \, \Omega/\text{sq} \), which is \( \sim 50 \) times lower than thermal reduction alone (\( 2.14 \times 10^6 \, \Omega/\text{sq} \)) under the same process conditions. The apparent increase in conductivity is most probably due to a higher concentration of \( sp^2 \) clusters, which leads to enhanced electrical transport via percolation [138]. Our sheet resistance is comparable to the lowest reported value for hydrazine treatment, followed by thermal annealing (\( \sim 4.3 \times 10^4 \, \Omega/\text{sq} \)) [120]; we note that our process is lower temperature and shorter exposure time. Further improvements in the

**Figure 6.8.** Micro Raman spectra (\( \lambda = 633 \, \text{nm} \)) of GO thin films. Spectra of original GO (red curve), GO reduced by thermal annealing in \( \text{Ar/H}_2 \) atmosphere (orange curve), GO reduced by Ar plasma (blue curve), and GO reduced by \( \text{Ar/H}_2 \) plasma (green curve) are shown. In the inset, the \( I(D):I(G) \) ratio is shown before and after reduction. All reduction was performed at atmospheric pressure, 150 °C for 30 min.
conductivity may be possible by optimizing the exposure time, discharge current, and sample distance.

We finally address the issue of hydrogenation – the exposure of GO (or reduced GO) to atomic hydrogen suggests that the sp^2 domains in the film could be hydrogenated, similar to what has been observed for graphene [127]. A recent report showed that the mechanism for plasma hydrogenation of graphene is electron irradiation of H_2O adsorbates rather than reaction with atomic hydrogen. Because in our case electrons (and ions) do not interact with the GO film, we do not believe hydrogenation of sp^2 groups occurs. This was verified by a simple test experiment where we treated CVD-grown graphene under typical conditions as our GO and observed no noticeable change in the chemical structure [See Figure 6.9]. Therefore, we infer that in our process the atomic

Figure 6.9. Micro Raman spectra (λ=633 nm) of pristine CVD-grown graphene (green curve) and graphene after exposure to remote plasma process (orange curve). Plasma exposure was carried out under typical conditions: 50/50 Ar/H_2, discharge current=10 mA, substrate temperature=150 oC, and process time=30 min.
hydrogen does not react with sp$^2$ groups in the GO film, and its main chemical pathway is reactions with sp$^3$ (oxygen functional) groups.
6.4 Summary

A chemically reactive, atmospheric-pressure microplasma has been developed for the non-equilibrium reduction of GO films at low temperature. The generation of atomic hydrogen, as verified by optical characterization of the plasma, allows effective removal of oxygen functional groups in GO films at temperatures as low as 70 °C. The process presented here opens the possibility of incorporating reactive chemistry for plasma reduction.
7.1 Overall summary

In this dissertation, we have developed a new chemical approach, termed plasma electrochemistry, to modify and assemble various types of nanomaterials: colloidal metal nanoparticles, metal nanoparticle/polymer films, nanowires, and reduced graphene oxide (rGO). In Chapter 2, we showed evidence of electron-transfer reactions at the plasma-liquid interface. The ability to initiate electrochemical reaction with gas-phase electrons opens a new direction for chemical and materials synthesis. This has led to in the reduction of dispersed metal cations in polymer films (Chapter 3 and 4) or metal moieties in a metallopolymers template (Chapter 5). Overall, our approaches to nanofabrication can be divided into three categories: (1) direct writing, (2) nanomasking, and (3) directed assembly. In Chapter 6, we extended this approach to the reduction of GO which requires chemical reduction; the introduction of hydrogen chemistry enabled the generation of atomic hydrogen to effectively react and remove stable oxygen functional groups in GO films.

Looking past these examples, there is much work left to be done. Applications of plasma electrochemistry have only scratched the surface and as this area continues to develop, we believe this approach will find better and larger applications. Some of our thoughts on where this research will go next are summarized below.
7.2 Plasma-liquid electrochemistry

Bimetallic nanoparticles: Recently, bimetallic nanoparticles have been actively studied because of their unique catalytic [166, 167, 168, 169] and optical properties [170, 171, 172] as a result of synergistic effects between the individual components. Preparation of size- and compositionally-controlled bimetallic nanoparticles remains a significant synthetic challenge. Plasma-liquid electrochemistry is potentially suitable since aqueous metal ions can be rapidly reduced in solution. In the future, we will explore the coreduction of metal ions (i.e. AuCl₄ and H₂PtCl₆) and evaluate the composition and structure of the as-synthesized material.

Graphene exfoliation: A dispersible form of graphene is attractive in order to use solution processing methods such as spin coated and ink jet printing to fabricate flexible electronic devices. As we showed in Chapter 6, one form of dispersible graphene is GO; however, the oxygen functional groups in GO are very difficult to remove. Alternatively, it may be possible to exfoliate graphene in solution without oxidizing by using surfactants to stabilize the graphene flakes in solution. We have recently explored the implementation of a plasma in the chemical exfoliation of graphene. Figure 7.1a shows illustrates the experimental set up. The basic idea is to operate a solid graphite (highly oriented pyrolytic graphite) as the anode of a plasma electrochemical cell and drive current through the electrolyte to force the graphite to exfoliate into solution. A surfactant in solution (sodium dodecyl sulfate) reacts with the graphite surface and also binds to the graphite flakes to stabilize in solution. Our preliminary results demonstrate
that graphene can be exfoliated by this approach [Figure 7.1b], but further studies are needed to optimize the process and characterize the material.

**Figure 7.1.** (a) Schematic of graphene exfoliation based on plasma electrochemistry. (b) The comparison for color change of the exfoliated graphene, (i) DI water, (ii) 80 °C of heating exfoliation for 1 hr, (iii) conventional electrochemical cell at 80°C for 1 hr, (iv) plasma electrochemical cell at room temperature for 5 hr, (v) plasma electrochemical cell at 80°C for 1 hr.
7.3 Towards nanofabrication

Our general goal is to transfer patterns at smaller scales using some of the techniques developed in this thesis. The developed techniques have their own advantages and disadvantages.

Direct writing: The size of patterns transferred by direct writing is currently limited by the size of the microplasma source. By reducing the size of this writing tool, for example by moving to tip-based writing with a carbon nanotube [173], we believe the size of the transferred patterns can be reduced from 100 μm to 1 μm.

Nanomasking: With the aid of lithographic masks, we have reduced the size of transferred patterns to less than 100 nm. This pattern size can be further reduced with improved masks. Focused ion beams (FIB) can be used to fabricate patterns with less than 10 nm size [Figure 7.2]. We are exploring the use of these masks to transfer patterns via plasma electrochemistry.

Directed assembly: Metallo-supramolecular polymer chemistry enables metal moieties to be assembled for direct reduction and formation of arrays of metal nanoparticles. One of the novel aspects of this approach is that the as-synthesized nanoparticles are well-dispersed since they are nucleated from the film rather than separately synthesized then dispersed in the polymer. We believe this material system can exhibit novel properties including high transmission and conductivity for flexible transparent electrode applications. In the future, we plan to fabricate electronic devices and characterize the
optical and electronic properties of the metallopolymer films after plasma electrochemical reduction.

Figure 7.2. SEM image of FIB patterned 3C-SiC membrane.
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