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It is entitled: Mass-Producible Nanotechnologies Using Polymer Nanoinjection Molding: Nanoparticle Assemblies, Nanoelectrodes, and Nanobiosensors

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Mass-Prodúcible Nanotechnologies Using Polymer Nanoinjection Molding: Nanoparticle Assemblies, Nanoelectrodes, and Nanobiosensors

A dissertation submitted to the

Division of Research and Advanced Studies
of the University of Cincinnati

in partial fulfillment of the
Requirements for the degree of

DOCTOR OF PHILOSOPHY (Ph.D.)

in the Department of Electrical and Computer Engineering
of the College of Engineering

April 30, 2009

By

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B.S., Department of Electrical & Computer Engineering and Computer Science, University of Cincinnati, Cincinnati, OH, 2003

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The objective of this research is the realization of mass-producible nanotechnologies, including nanoparticle assemblies, nanoelectrodes, and nanobiosensors. In order to achieve this goal, mass-producible nanofabrication methods were developed and fully characterized. The newly developed fabrication techniques were then applied for the realization of an electrochemical nanobiosensor that is combined with custom detection circuitry for ultra-sensitive detection of biomolecules.

The foremost accomplishment of this work is the establishment of a new nanofabrication platform that couples the precision and throughput of polymer injection molding with the simplicity of template-driven assembly. High-throughput nanoinjection molding technology was developed, characterized, and applied for the fabrication of polymer substrates with nanostructured surfaces. Electron-beam lithography and metallization techniques were used for the development of a nanostructured mold, which was subsequently utilized to create negative polymer replicas by injection molding with cyclic olefin copolymers (COC). The nanostructured polymer chips were then used as templates for the patterning of nanomaterials using the newly developed nano-assembly technique of deposition with selective removal. Template-driven assembly of various sizes and types of nanoparticles was demonstrated in one-dimensional (1D) and two-dimensional (2D) patterns over large areas. Template dimensions such as width and depth were used to control the assembled nanoparticles, including quantity and type of nanoparticles in the assembly. The nanofabrication technique of deposition with selective removal using polymer templates was also used for the patterning of multiple types of metals for the formation of nanoelectrodes in both 1D and interdigitated array formats.
The newly developed fabrication techniques were applied for the realization of an electrochemical nanobiosensor using nano interdigitated array (nIDA) electrodes on the polymer template. A hybrid detection circuit was custom-designed and implemented with the nIDA for amperometric detection of redox species poly-aminophenol (PAP). When compared with a micro interdigitated array (mIDA) biosensor, the nIDA biosensor showed improved current output and improved detection limit.

The technologies developed in this work may have an immediate impact on commercial applications of nanotechnology due to the low-cost and high-throughput processing techniques that were generated and used. Additionally, the newly established nanofabrication platform may be useful for the assembly of a wide range of materials for numerous applications, including novel optical and electronic devices.
ACKNOWLEDGMENTS

This dissertation is the product of an extremely exciting, challenging, and ultimately rewarding experience of pursuing my doctorate in electrical engineering. During this process, I experienced growth in a number of technical, professional, and personal areas, which has deeply impacted all aspects of my life. It goes without saying that this dissertation would not have been possible without the support of many individuals and groups that have helped me along the way.

I have been fortunate to have Dr. Chong H. Ahn serve as my dissertation advisor and professional mentor for the past six years. His technical guidance, support, and encouragement have been instrumental in developing my skills as a researcher, and for that I am deeply grateful. In addition to being a top researcher in the BioMEMS field, he is also a passionate teacher and educator, and I have learned a great deal from him about what it takes to inspire others to achieve their goals and dreams.

I am also extremely appreciative of Dr. Tom Mantei, Dr. Marc Cahay, Dr. Mark Schulz, and Dr. Bill Heineman, who have provided their time and technical expertise while serving on my dissertation committee. Their suggestions and advice have greatly improved the quality of this work, and for that I am very thankful.

My graduate studies were supported by a number of funding sources that allowed me to focus on my courses and research without worry over financial matters. I am grateful to the Department of Electrical & Computer Engineering for providing a Teaching Assistant position during my first year of study; as well the College of Engineering for providing a scholarship that covered my tuition throughout my doctoral program. I am also appreciative of funding received from the National Science Foundation through NSF Grants 0139312 and 0622036, which supported me for the remaining portion of my studies and research.
A particularly unique component of my doctoral program was my participation in Project STEP, which allowed me to bring my engineering expertise into high school classrooms for the creation of hands-on activities. This experience has had a profound impact on my professional and career interests, and I am deeply appreciative of the opportunity to participate in this program. I am especially thankful for Dr. Karen Davis, Dr. Ted Fowler, Dr. Suzanne Soled, and Dr. Anant Kukreti, who provided support and mentoring throughout my involvement in Project STEP.

Without a doubt, one of the best experiences of graduate school has been the opportunity to learn from, and work alongside, a fantastic set of colleagues in the Microsystems and BioMEMS Laboratory. Chuan Gao, Xiaoshan Zhu, and Jaephil Do were all extremely helpful in training me in micro- and nanofabrication, which provided the basis for much of my work. I am also deeply indebted to Se Hwan Lee, who provided technical and professional guidance as well as being a great friend and mentor. Many thanks are in order for my classmates Matt Estes, Peiming Wu, and Zhiwei Zou, who joined the lab at the same time as I and provided a great working environment over the years. Gentlemen, it was a pleasure to work with you. I am also very appreciative of Andrew Browne, who was a great sounding board for ideas and an excellent collaborator, and Joon Sub Shim, whose diligence and work ethic is an example for all. To all the other Ahnlab members I have worked alongside, including Aniruddha Puntambekar, Chien-Chong (Red) Hong, Clayton Sippola, Junhai Kai, Jungyoup Han, Rong Rong, Chunyan Li, SooHyun Lee, Kang Kug Lee, WooSeok Jung, Eric MacKnight, Nathan Hadlock, Ashwin Samarao, Phalgun Myneni, Alok Jain, Shilpa Thati, and Robert Cole, I offer my sincere thanks for everything you did to make my experience so rewarding.
Anyone who has ever worked in a research environment knows what a valuable resource a technical staff can be, and our clean room staff at UC is no exception. I am very grateful for the support and assistance offered by Jeff Simkins, Ron Flenniken and Dr. Robert Jones, whose training and technical advice accelerated my development as a researcher while also increasing my productivity.

My family and friends have been especially supportive of my graduate endeavors, and I very much appreciate their love and encouragement. In particular, I thank my parents for fostering my passion for engineering and encouraging me to achieve my dreams. I also wish to thank my friends at St. Monica-St. George Church, who have helped me grow spiritually over the past several years.

Last, and certainly not the least, I thank my wife Andrea, who’s love and support has truly been a blessing over the course of my graduate work. Throughout my studies, she has been my rock of strength, making many sacrifices to allow me to pursue my dreams. I cannot find words that can describe how grateful I am to have her in my life.
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<td>Polycarbonate</td>
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<td>SBS</td>
<td>Styrene-Butadiene Block Copolymer</td>
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<td>COC</td>
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CHAPTER 1

INTRODUCTION
1.1 Research Motivation

The field of nanotechnology can trace its origin to a talk given by Richard Feynman in 1959, in which he described the manipulation of matter at the atomic and molecular level [1, 2]. Speaking at the annual meeting of the American Physical Society, Feynman introduced several prescient concepts:

“I would like to describe a field, in which little has been done, but in which an enormous amount can be done in principle... What I want to talk about is the problem of manipulating and controlling things on the small scale... It is a staggeringly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction.” [1]

While the tools existing in the mid-20th century were insufficient to produce such results, Feynman’s vision of molecular manufacturing turned into reality in the latter half of the 20th century with the development of nanofabrication equipment and techniques. For example, the invention of the scanning tunneling microscope (STM) and its use in 1990 to manipulate individual xenon atoms was a major landmark in the development of nano-scale technologies [3]. Since that time, there has been explosive growth in the research and development of tools for nano-scale fabrication.

The increased interest in materials, structures, and devices with nano-scale features (Figure 1.1) is due to a number of benefits that can be obtained from the ultra-small scale, which are largely dependent on the specific application. For example, the performance of electronic
devices has been greatly improved as components, such as the gate-length of the transistor, are reduced to the nano-scale, resulting in improved switching speed and increased integration density [4]. In the fields of medicine and biology, the development of tools with nano-scale features, such as functionalized nanoparticles, can give unprecedented access to the inter-cellular environment for diagnosis and therapy [5]. In addition to the simple down-scaling of existing technologies, several phenomena have been observed in nanomaterials that have enabled entirely new devices to be developed with significantly improved performance. For example, carbon nanotubes (CNTs) have demonstrated improved mechanical, thermal, and electrical properties [6] which have been applied for field-effect transistors (FETs) [7], light emission devices [8] and biosensors [9].

Figure 1.1. Relative scales of biological and human-made structures from meter-scale to nanometer-scale.
A particular area of interest in nano-scale science and technology is the development of nanoparticle assemblies on solid substrates for applications in electronic, optical, and biosensing devices [10, 11]. The primary reason for this interest is that nanoparticles exhibit properties that are different than that of bulk materials, leading to improved performance and the development of entirely new devices. For example, the distribution of electronic states in nanoparticles differs from that of bulk material, resulting in a quantum confinement effect that is size dependent [12]. Thus the bandgap of a semiconducting nanoparticle, which determines its emission wavelength, can be controlled by the diameter of the nanoparticle, enabling the precise tuning of optical characteristics for use in light emitting diodes (LEDs) [13]. With regard to metal nanoparticles, the quantum confinement effect can be utilized to capture and release individual electrons from a nanoparticle, providing a route to single electron transistors [14].

The optical properties of nanoparticle assemblies are also very interesting for device applications. For instance, if nanoparticles can be assembled into a periodic structure with control over the particle dimensions and spacing, the resulting periodic modulation of the dielectric constant gives rise to a forbidden region in the photonic band structure [15]. This forbidden gap excludes optical modes that are associated with a range of frequencies, thus allowing for the manipulation of light for optical-based communication devices. It is expected that nanoparticle assemblies will therefore play an important role in the development of optical integrated circuits that will result in further improvements in processing and communication technologies [16]. Another major area of application for nanoparticle assemblies is biorecognition and biosensing [17]. Due to their large surface area-to-volume ratio and high surface free energy, nanoparticles can adsorb biomolecules strongly and thus are easily
functionalized for biorecognition [18, 19]. After assembly on solid substrates, functionalized micro/nanoparticle arrays have been demonstrated for highly sensitive biosensors in labeled [20] and label-free formats [21].

There has also been significant interest in the fabrication of nanoelectrodes and nanoelectrode arrays on solid substrates [22]. By reducing the width and/or spacing of electrodes to the nano-scale, improved performance can be achieved for a range of devices and applications, including the development of molecular-scale electronics [23-25]. An obvious benefit of nano-scale electrodes is the increased integration density for electronic devices afforded by the reduction in dimensions [4]. By fabricating devices, interconnects, and traces at nano-scale width and pitch, more room is available on the chip surface for additional devices and functionalities. Additionally, chip sizes can be further reduced for applications such as wearable or implantable devices [26].

Nanoelectrodes can also be used to improve the performance of specific devices. For example, organic electronic devices, such as organic field-effect transistors (OFETs), are attractive options for low-cost computing due to their inexpensive fabrication and materials, but they remain infeasible due to the high operating voltages that result from poor charge transport in the organic layer [27]. By using nanoelectrode arrays as the source and drain components for OFETs, the reduced transit path for charges will permit lower operating voltages and improved switching speed, allowing the realization of low-cost bioelectronics [28].

Another major application of nano-scale electrode arrays is the creation of ultra-sensitive biosensors for integration with lab-on-a-chips. Since the first demonstration by Manz in 1990 [29], lab-on-a-chips have been extensively researched and developed for use as miniaturized analysis systems [30, 31]. Combining fluid handling components, such as microchannels and
valves, with sensors for the detection of biomolecules, these lab-on-a-chips offer several advantages including low sample and reagent consumption, reduced waste, faster reaction times, and portability [32]. In recent years, research has focused on the development of electrochemical sensors, which are attractive for lab-on-a-chips due to their simple excitation and detection requirements, with improved performance for the trace detection of biomolecules [33]. One approach that received considerable interest has been the use of microelectrodes in an interdigitated array (IDA) format due to their current enhancement property [34]. In this method, two interdigitated electrodes serve as the anode and cathode, respectively, for the detection of electrochemically active species. The anode is held at the oxidation potential of the target species and the cathode is held at the corresponding reduction potential. During the reaction, the species to be detected reacts with one electrode and then diffuses to the other electrode where the reverse reaction takes place. For example, if the target molecule reacts with the anode it will be oxidized and then reduced when it reacts with the cathode. Thus the species for detection diffuses back and forth between the electrodes where it is reduced and oxidized in cycle called redox cycling [35, 36]. As electrons are exchanged between the electrodes and the target species, a steady-state limiting current is developed at the electrodes, which is proportional to the concentration of the species in solution and the geometry of the IDA electrodes. This current can be modeled as shown in Equation 1:

\[
I_{\text{lim}} = m b n F C_{\text{spe}} D [0.637 \ln \left( \frac{2.55(w + g)}{g} \right) - 0.19 \left( \frac{g}{w + g} \right)^2] \quad (1)
\]

where \( m \) is the number of electrode fingers, \( b \) is the electrode finger length, \( n \) is the number of electrons involved in the reaction, \( F \) is Faraday’s constant, \( C_{\text{spe}} \) is the concentration of the redox species, \( D \) is the diffusion coefficient of the redox species, \( w \) is the width of the electrode fingers, and \( g \) is the gap between the electrode fingers [37, 38].
The critical factor for improving the detection limit of IDA-based electrochemical sensors is the gap between the electrode fingers [39]. As the gap between IDA electrodes is decreased from the micro-scale (mIDA) to the nano-scale (nIDA), the majority of species generated at one electrode will be collected at the other electrode [36]. This increase in redox cycling efficiency results in a significant enhancement of the limiting current, which enables the detection of lower concentrations of biomolecules [39]. The use of nano interdigitated arrays (nIDA) can thus significantly improve the performance of electrochemical sensors for trace detection of biomolecules in lab-on-a-chips.

As a result of the significant advances offered by nanotechnologies such as nanoparticle assemblies, nanoelectrodes, and nanobiosensors, attention has turned to the development of devices for commercial markets [40]. For example, the National Nanotechnology Initiative (NNI), which is a program established in 2001 to coordinate nanotechnology research and development in the United States, has identified the transfer of nanotechnologies into products for commercial and public benefit as one of its four major goals [41]. However, in order for these nanotechnologies to successfully transition from research laboratories to commercial products, fabrication techniques must be developed that can manufacture nano-scale structures and devices at mass-production levels while maintaining low costs. Unfortunately, the majority of nanofabrication techniques that have been developed to date involve the fabrication of small quantities of nanodevices at relatively high unit cost. Therefore, the development of nanomanufacturing techniques for large-scale production of low-cost nanotechnologies is highly desired.
1.2 Review of Previous Work

Nanoelectrode Fabrication

One of the most popular methods for producing nanoelectrodes involves direct-write patterning techniques, such as electron beam lithography (EBL). In EBL, a beam of electrons is scanned across a substrate that has been coated with an electron-sensitive thin-film or resist, such as polymethylmethacrylate (PMMA) [42]. For a positive (negative) resist, areas of the film that are exposed to the electron beam are then removed (retained) by immersion in a developer solution. Since the electron beam can be controlled by pattern-generating software, and the beam itself can be focused to a diameter of a few tens of nanometers, EBL can be used to create sub-100 nm features in a wide range of shapes in resists on top of substrates. The patterned resist can then be used as a mask to transfer the pattern to the substrate surface by etching, or the pattern can be used to create structures on top of the substrate. For example, metal can be deposited on the resist pattern and removed by liftoff process to create nanoelectrodes [43, 44]. While EBL has been used extensively in research settings, it remains impractical for use in large-volume production of patterns and devices as a result of several factors. Since each pattern must be produced serially rather than in parallel, EBL results in low-throughput processing that is not suitable for mass-production environments. Additionally, EBL must be performed on a conductive substrate, such as silicon (Si), which increases the cost per device and precludes the use of low-cost polymers as substrate materials unless they are modified with a metallic surface layer.

To overcome the throughput constraints of direct-write techniques, the research group led by Stephen Chou developed a method for nanofabrication that involves the simultaneous patterning of an entire wafer in one process step [45]. Known as Nanoimprint Lithography (NIL)
[46-48], this technique involves the pressing of a master mold, which contains nano-scale surface features, into a thin polymer film on top of a substrate (Figure 1.2). After removal of the mold, the thin polymer film contains a pattern corresponding to the mold features. As with patterns generated by EBL, the NIL patterns can be transferred to the substrate by etching, or the pattern can be used in a lift-off process for the creation of nanoelectrodes.

![Figure 1.2](image_url)

Figure 1.2. Nanoimprint Lithography: (a) schematic diagram of fabrication method; (b) SEM image of 100 nm patterns in PMMA fabricated by NIL; (c) SEM image of nano-scale metal patterns after deposition and liftoff. Images adapted from [45].

NIL has been demonstrated with sub-25 nm resolution; the limiting factor is the development of the master mold itself, which is usually fabricated by EBL. Therefore, after an initial investment in a quality master mold, minimal equipment is required to transfer the pattern to the substrate. Additionally, since it allows parallel processing of nano-scale patterns, NIL significantly improves the throughput of device fabrication over EBL. However, with typical imprinting cycle times on the order of 10-20 minutes, NIL is still not ideal for the mass-production of nano-scale electrodes for large-volume commercial applications [47, 49, 50].
A significantly different approach to nanoelectrode fabrication was described by Menon and Martin [51]. In their method, a porous membrane (track-etch polycarbonate) is coated with a gold film by electroless plating. Thus, the membrane pores become filled with gold, which forms nanowires that traverse the full-thickness of the membrane. Additionally, both the top and bottom surfaces of the membrane are also coated with a thin gold film during the plating process. Subsequently, one of the gold surfaces (either the top or bottom) is removed by applying an adhesive tape, thus revealing the tips of the gold nanowires that traverse the membrane (Figure 1.3). After making electrical contact to the remaining gold film, the nanoelectrode array can be electrically addressed. This method provides a simple, low-cost approach to nanoelectrode formation, however it does not allow for direct control over the shape of the nanoelectrodes, which are determined by the porous membrane.

Figure 1.3. Nanoelectrode fabrication by electroless plating in porous membrane, adapted from [52].
Assembly of Nanoparticles

A variety of techniques have been developed for the assembly of nanoparticles on solid substrates, which can be placed in broad categories of direct manipulation [53] and solution-based techniques [54]. Eigler and Schweizer used a scanning tunneling microscope (STM) to manipulate individual xenon (Xe) atoms through a combination of electrostatic and Van der Waals forces [3]. The particles were dragged across the surface of a nickel (Ni) substrate and placed in desired positions to spell the name of the researchers’ employer, IBM (Figure 1.4). In a similar approach, Resch and coworkers used an atomic force microscope (AFM) to push and stack gold nanoparticles into three-dimensional (3D) structures on a Si substrate [53]. While these methods marked major advancements in nano-scale manufacturing, the direct manipulation of individual nanoparticles with the tip of an STM or AFM is not currently suitable for large-volume production of nanodevices as a result of their inherently low-throughput, serial processing formats.

Figure 1.4. Manipulation of individual atoms using STM: (a) schematic diagram showing assembly procedure; (b) STM image of Xe atoms on Ni surface prior to assembly; (c) STM image of Xe atoms that have been manipulated by STM to form the acronym ‘IBM’. Images adapted from [3].
As an alternative to direct manipulation approaches, a wide range of solution-based techniques have been reported for the assembly of nanoparticles on solid substrates, including Langmuir-Blodgett techniques [55], controlled evaporation [56], and chemical linkage [57]. In each of these approaches, nanoparticles can be uniformly deposited across a substrate surface. However, the formation of specific nanoparticle assembly shapes can be challenging unless the substrate is pre-patterned prior to the assembly of nanoparticles [11]. Yin and coworkers described a method for the assembly of micro- and nanoparticles using a patterned substrate and an applied capillary force (Figure 1.5) [58]. In this approach, often referred to as template-assisted self-assembly (TASA) [58-63], a slug of solution containing particles is flowed over a substrate that has micro/nano patterned surface, which is called the template. As the slug of solution is removed, its receding meniscus causes a capillary force to be exerted on the particles, causing them to be trapped in the template patterns while also cleaning the top surface of the template. This allows the formation of specific nanoparticle assembly shapes, which are determined by the template patterns. A disadvantage of this approach is the complex interplay between the capillary force, the nanoparticle surface charge, and charges existing on the template surface. These factors can result in unsuccessful assembly if not properly accounted for and require special consideration regarding substrate material and nanoparticle type. Additionally, the effects of Brownian motion become more significant as the nanoparticle size is reduced, which may negatively impact the effects of capillary force and lead to unsuccessful assembly.
Another factor preventing the application of template-based assembly methods to mass-production of nanodevices is the lack of an appropriate fabrication method for the templates, which should be manufactured at low-cost using high-throughput production techniques while maintaining the nano-scale resolution of the desired pattern shape. Templates for nanoparticle assembly have been fabricated by a range of techniques. Misner and coworkers used the porous structure of polystyrene-polymethylmethacrylate (PS-PMMA) diblock copolymers to form a template layer on top of a Si substrate [64]. The major limitation with this approach is the random structure of the template, which provides little control for the designer to create appropriate pattern structures for device applications. Improved control over pattern shape can be achieved by using optical lithography to create template patterns in a resist on top of a substrate, as demonstrated by Li and coworkers [65]; however, the resolution is limited by the wavelength of the light source. Interference lithography has been applied to make sub-micron patterns in resists, as demonstrated by Juillerat and coworkers [60], but this method is typically limited to producing periodic patterns and cannot be easily applied for a wide range of template shapes. The aforementioned problems of pattern shape and resolution can be overcome by using
EBL. Cui and coworkers used EBL for the creation of 50 nm template patterns in resist on top of a Si substrate, and they used their template for the assembly of gold (Au) nanoparticles [66]. However, as described earlier, EBL is a low-throughput and expensive process that is not suitable for mass-production of templates. Improved throughput for fabricating a range of nano-scale patterns using NIL has been demonstrated by Chou and coworkers [45], and has been applied for creating templates for assembly by Maury and coworkers [50]. However, typical cycle times on the order of 10-20 min for imprinting limits its application in mass-production settings [47, 49, 50]. Therefore, the development of high-throughput fabrication techniques for templates to be used for assembly of nanoparticles is desired so as to allow nanoparticle-based devices to be fully realized for commercial applications.

*Polymer Injection Molding*

Injection molding is a technology that has been used to fabricate plastic parts for a variety of commercial applications, including the automotive industry, household items, electronics, and toys [67]. In this process (Figure 1.6), a thermoplastic polymer is melted and injected at high pressure into a cavity containing a mold structure. After filling the cavity and mold patterns, the polymer is allowed to cool before being ejected, and the cycle is then repeated. With cycle rates at or above one chip/minute, injection molding can be used for the high-throughput production of plastic parts. Additionally, the low cost of polymer materials makes the process suitable for mass-production of polymer structures for commercial products.

Injection molding has become a popular tool in a variety of research fields due to its ability to replicate mold structures with micro- and nano-scale precision [68]. Mönkkönen et al. used injection molding with polycarbonate (PC), styrene-butadiene block copolymer (SBS),
PMMA, and cyclic olefin copolymer (COC) to produce features down to 200 nm [69]. Macintyre and Thoms demonstrated sub-100 nm features in PC using molds fabricated by EBL [70]. Schift et al. were able to produce 25 nm structures in PC using molds fabricated by EBL, and demonstrated mold lifetimes on the order of hundreds of injection cycles [71]. Injection molded micro- and nanostructures have been used for a range of applications, including microfluidic channels [72], titer plates [73], and compact discs [71].

Figure 1.6. Polymer injection molding: (a) schematic diagram of injection molding process, adapted from [68]; (b) SEM image of micro/nano structured PC produced by injection molding, adapted from [69].

1.3 Research Objectives

There is a clear need for a new nanofabrication approach that can achieve nano-scale resolution in a high-throughput methodology for production of nanoparticle assemblies and nanoelectrodes. To accomplish this objective, a new nanofabrication platform is established that couples the precision and throughput of polymer injection molding with the simplicity of template-driven assembly. High-throughput nanoinjection molding technology is used to produce
polymer templates with nanostructured surfaces. The nanotemplates are then used in a newly
developed nano-assembly technique of deposition with selective removal for the fabrication of
nanoparticle assemblies and nanoelectrodes. Since both the template fabrication and subsequent
use for patterning of nanoelectrodes and nanoparticle assemblies are high-throughput, low-cost
techniques, this approach allows the mass-production of nanodevices for commercial
applications, such as nanobiosensors.

To achieve the research objectives, four research tasks were defined:

(1) The development of polymer nanotemplates using nanoinjection molding

(2) The assembly of nanoparticles on polymer nanotemplates

(3) The patterning of nanoelectrodes on polymer nanotemplates

(4) The development of electrochemical nanobiosensor using nano interdigitated array on
polymer nanotemplates.

Each of these research tasks is addressed in this thesis. Chapter 2 focuses on the
development of nanoinjection molding technology and its use for fabricating polymer
nanotemplates. The full fabrication process is described and characterized, and results are
presented for injection molding of cyclic olefin copolymers (COC). The fidelity of pattern
transfer from the nanostructured mold to the polymer template patterns is studied and the
durability of the mold as a function of feature size and number of injection molding cycles is
presented.

Chapter 3 introduces the concept of nano-assembly by deposition and selective removal
of nanoparticles on the polymer nanotemplate. The fabrication process is characterized and
results are demonstrated for multiple types and sizes of nanoparticles in one-dimensional (1D)
and two-dimensional (2D) patterns over large areas. Additionally, template dimensions such as width and depth are used to provide control over the assembled nanoparticles, including quantity and type of nanoparticle in the assembly.

In Chapter 4, a modified version of the nano-assembly technique is presented for the patterning of metals on the polymer template, resulting in the formation of nanoelectrodes. The nanoelectrode fabrication process is demonstrated and characterized for both silver and gold electrodes in 1D and interdigitated array (IDA) format.

In Chapter 5, the nanoelectrode fabrication technique is applied for the development of an electrochemical nanobiosensor using nano interdigitated array (nIDA) on polymer substrate. A hybrid detection circuit is custom-designed and implemented with the nIDA for amperometric detection of redox species poly-aminophenol (PAP). Results are presented and compared with micro interdigitated array (mIDA) sensor.

The thesis concludes with a discussion of the benefits and limitations of the developed technologies and fabrication techniques, as well as suggestions for future work, which can be found in Chapter 6.
CHAPTER 2

DEVELOPMENT OF POLYMER NANOTEMPLATES USING NANOINJECTION MOLDING TECHNOLOGY
2.1 Introduction

There exists a strong need for the development of templates that allow for rapid assembly of nanostructures, such as nanoelectrodes and nanoparticle assemblies. Central to this aim is the development of a method for producing the templates in a high-throughput, low-cost approach, while maintaining the nano-scale precision required for the subsequent assembly of nanostructures. Templates for nano-assembly have been demonstrated through the use of diblock copolymers [64], interference lithography [60], and nanoimprint lithography [50]; however none of these approaches allows the high-throughput fabrication of templates with nano-scale control over pattern shapes.

On the other hand, polymer injection molding is a technology that is ideally suited for such an approach because of its rapid fabrication capability and its potential for production of nano-scale structures [74]. In this process (Figure 2.1), a thermoplastic polymer is melted and injected at high pressure into a cavity containing a mold structure [67]. After filling the cavity, including the mold patterns, the polymer is allowed to cool before being ejected and the cycle is repeated. Thus, the polymer substrate contains surface structures that are negative replicas of the mold features (ridges and posts on the mold surface become trenches and pores on the polymer surface, respectively). With cycle times approaching 1 chip per minute, this method is highly suitable for mass-production settings. Additionally, the use of inexpensive polymer materials further reduces the overall cost of the process for large-volume production of templates.
Figure 2.1. Polymer injection molding: (a) molten polymer is injected into cavity containing mold structure; (b) the polymer fills the cavity and conforms to the mold features; (c) after cooling, the polymer structure is ejected and the cycle repeated.

2.2 Mold Development

2.2.1 Design

The ultimate goal of an injection molding process is the replication of mold structures in a polymer material. Since the resulting polymer parts are negative replicas of the original mold structures, the development of the mold for injection molding is a critical component of a successful process.

A popular approach for injection molding involves a replaceable mold disk technique [72]. In this methodology, the molding block of an injection molding machine is modified to allow the insertion of a smaller part that contains the mold features to be replicated. As a result, the mold can be easily replaced with another pattern without having to re-fabricate the entire molding block, thus saving time and reducing costs [75]. Additionally, the smaller size of the replaceable mold disk facilitates the use of planar micro/nano fabrication processes that are typically incompatible with large structures such as the molding block.
A replaceable mold disk technique was previously developed at the University of Cincinnati by Choi et al. [76]. In this method (Figure 2.2), a circular mold disk (3 inch diameter, 1.6 mm thick) is used as a substrate for planar microfabrication of mold structures. The mold disk is then inserted into a custom-designed molding block of an injection molding machine (BOY 22M-A, BOY Machines) for replication in plastic materials. The thickness of the mold insert and the cavity dimensions of the molding block are designed to produce 1 mm thick polymer chips after injection molding. In the previous works [76, 77] micro-scale structures were produced on the mold disk surface by thick-film photolithography and electroplating techniques. In this work, a new fabrication process was developed to achieve nano-scale structures on the mold disk surface.

![Image](https://via.placeholder.com/150)

**Figure 2.2.** Replaceable mold disk technique for polymer injection molding, adapted from [75].

The most important factor in determining the resolution of an injection molding process is the size of features on the mold. Therefore, the development of the mold structures with nano-scale dimensions is a critical aspect of a successful nanoinjection molding technique.
Additionally, the background surface roughness of the mold surface must be significantly smaller than the feature size of the mold structures, or the mold features will be indistinguishable from the substrate surface. Thus, the major requirements for the mold for nanoinjection molding include a planar substrate with an ultra-smooth surface on which nanostructures can be patterned.

Nickel (Ni) was selected as the mold disk material due to its potential for a polished surface and its mechanical strength for molding [76]. To produce nano-scale patterns on the Ni surface, electron beam lithography (EBL) was selected due to its sub-100 nm precision and capacity for generating a variety of pattern shapes. For metallization of the patterned substrate, a liftoff process was selected due to its capability for depositing a wide range of metals with nano-scale resolution.

### 2.2.2 Fabrication

The integrated fabrication process for producing a mold with nano-scale features for injection molding is shown in Figure 2.3 [78]. The process consists of 3 major steps: (1) Lapping/polishing of Ni disk to create mirror finish surface; (2) EBL on the Ni disk to create nano-scale patterns in a resist; (3) metallization of the nano-scale patterns by evaporation and liftoff.
To achieve a planar and smooth surface to serve as the mold substrate, a lapping and polishing procedure was used for the Ni disk. Chemical and mechanical lapping processes are widely used in industry for surface treatment [79]. In a typical procedure, an abrasive is used in combination with a rotating plate to mechanically lap the substrate surface in order to achieve planarity and low surface roughness. The procedure begins with the application of a coarse abrasive before proceeding to finer abrasives, with the final step involving the application of a polishing solution.

A Ni disk (3 inch diameter, 1.6 mm thick) was lapped using a PM5 Precision Lapping and Polishing Machine (Logitech, Glasgow, Scotland), as shown in Figure 2.4. The cast-iron lapping plate for the PM5 was pre-conditioned prior to use to ensure planarity. A cast-iron
conditioning block was used with calcined alumina (3 µm) abrasive solution (Lapmaster International, Morton Grove, IL) for 1 hour at a spin rate of 30 revolutions per minute (RPM). The Ni disk was then mounted on a glass chuck and loaded onto a lapping jig by applying a vacuum pump (0523-V3-SG588DX, Gast Manufacturing). Calcined alumina (3 µm) solution (Lapmaster International, Morton Grove, IL) was applied to the Ni disk for 1 hour at a 30 RPM spin rate. After rinsing with de-ionized water, 3 µm cerium oxide solution (Lapmaster International, Morton Grove, IL) was applied to the Ni disk for 1 hour at 70 RPM. For the final polishing step, colloidal silica solution (Allied High Tech Products, Rancho Dominguez, CA) was applied to the Ni disk for 30 minutes at 70 RPM.

Figure 2.4. Surface treatment for the Ni disk: (a) Logitech PM5 Precision Lapping and Polishing Station at the University of Cincinnati; (b) schematic diagram of lapping/polishing configuration.

After the Ni disk has been polished, it is used as a substrate for patterning with electron beam lithography (EBL). EBL is a technique that has been widely used for creation of nano-scale patterns, primarily for the creation of high-resolution masks for optical lithography and for
prototyping of semiconductor electronic devices [80]. In this approach, a substrate to be patterned is first coated with an electron-sensitive thin-film or resist. The resist-coated substrate is then loaded into vacuum chamber where it is positioned underneath an electron gun through the use of a precision motor-controlled stage. A column is used to focus the beam of electrons emanating from the gun, and a computer is used to control the beam so as to scan it across the sample surface. After exposing the sample, the substrate is removed from the chamber and placed in a developer solution. For a positive resist, areas of the resist that are exposed to the electron beam become soluble in the developer, and are thus removed. For a negative resist, areas of the resist that are exposed to the electron beam become insoluble in the developer, and thus remain. Since the electron beam can be focused to a diameter of a few tens of nanometers, EBL can be used to create nano-scale patterns in the resist layer on top of the substrate. Subsequently, the nano-scale pattern can be transferred to the substrate by etching or the deposition of metals with a liftoff process [42].

EBL was performed using the Raith 150 System (Raith GmbH, Dortmund, Germany) at the University of Cincinnati (Figure 2.5). Electron-sensitive positive resist polymethylmethacrylate (PMMA, MicroChem 495 A6) was spin-coated on the Ni substrate to a target thickness that was double the thickness of the metal to be deposited. After baking on a 180 °C hotplate for 2 minutes, the PMMA-coated Ni was exposed using the Raith-150 using the conditions shown in Table 2.1

After exposure, the resist was developed in 1:3 methylisobutyl ketone (MIBK): isopropyl alcohol (IPA) solution for 30 seconds. The development process was stopped by placing the patterned substrate in IPA solution for 30 seconds and then drying in nitrogen flow. To remove residual resist after development, the substrate was placed in a reactive ion etcher (RIE, March
CS-1701, March Plasma Systems, Concord, CA) for oxygen plasma treatment at 20 sccm and 70 W for 10 seconds. Evaporation of metal (Ni or Ti) was achieved with a Temescal FC1800 E-beam Evaporator, with the deposited metal film thickness specified as 50% of resist thickness. Liftoff was achieved by placing the substrate in an acetone bath for 1 hour.

![Image](image_url)

(a)       (b)

Figure 2.5. Electron beam lithography: (a) Raith 150 EBL system at the University of Cincinnati; (b) schematic diagram of EBL system and components.

Table 2.1. Exposure conditions for Raith-150 EBL.

<table>
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<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerating Voltage</td>
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</tr>
<tr>
<td>Aperture</td>
<td>30 µm</td>
</tr>
<tr>
<td>Area Dose</td>
<td>100 µC/cm²</td>
</tr>
</tbody>
</table>
2.3 Polymer Nanotemplates

2.3.1 Optimization of Nanoinjection Molding Process

Once the nanostructured mold has been fabricated, it is used for replication of polymer templates by nanoinjection molding (Figure 2.6) [74, 78]. In order to achieve nano-scale pattern transfer from the mold to the polymer templates, previously reported micro- and nano-scale injection molding processes were reviewed and optimized.

![Figure 2.6. Schematic diagram of nanoinjection molding process [78].](image)

An injection molding process consists of several key components and steps (Figure 2.7) [67]. First, a polymer material, typically in pellet or powder form, is loaded into the hopper on the injection molding machine. The polymer is then fed into a plasticizer, which contains a screw and heating elements. As the polymer material is grinded by the screw, significant heat is generated from the friction and the heating elements, which causes the polymer to be melted. The screw is then used as a piston to force the molten polymer from the plasticizer through a nozzle into the mold cavity. The molten polymer fills the entire cavity, including the mold
features, and is allowed to cool. After cooling is complete, the cavity is opened and the solidified polymer is ejected. The cycle is then repeated [67].

Figure 2.7. Schematic of typical injection molding system, adapted from [72].

There are several critical factors that should be considered when optimizing an injection molding process, including polymer selection, mold temperature, injection pressure, and flow rate. The first step is to select the polymer to be used for injection molding. A variety of polymers have been demonstrated for injection molding, including polycarbonate (PC) [70], polymethylmethacrylate (PMMA) [69], and cyclic olefin copolymer (COC) [76]. COC was selected for this work due to its superior material properties for injection molding, including the capacity for injection at high flow rates, as well as its lower viscosity, which leads to improved filling and replication of mold features [75]. Additionally, COC is resistant to polar solvents, such as acetone and methanol, and thus is suitable for use in typical microfabrication processes after injection molding is complete [75].

Another important consideration for injection molding is the temperature for the process. When the molten polymer is injected into the mold cavity, it is desirable for the melt to continue
to flow until it fills the entire cavity, including all of the mold features. If the mold and cavity are
maintained at a temperature significantly lower than the glass transition temperature ($T_g$) of the
polymer, the melt may begin to freeze before completely filling the mold structures, leading to
pattern distortion in the replicated polymer [81]. For macro-scale injection molding, this is not a
significant consideration, and thus mold temperatures are typically maintained below $T_g$ in what
is known as a “cold cavity” process [72]. However, as the size of the mold features is reduced to
the micro- and nano-scale, the mold should be heated to a temperature at or above the polymer
$T_g$ so as to facilitate the mold filling. The disadvantage of this approach is that the injected
polymer must be given more time to cool before being ejected, which increases the cycle time
for the process from a few seconds (for macro-scale features) to around 1 minute (for micro/nano
features) [72].

It is also important to consider the injection pressure and flow rate of the injection
molding process. Increasing the injection pressure facilitates the complete filling of mold
patterns, thus improving the fidelity of replication. Additionally, increasing the polymer flow
rate should allow the polymer to fill the entire cavity more quickly, thus reducing the distortion
related to premature freezing. However, if both the injection pressure and flow rate are
significantly increased, there is a potential for mechanically damaging the mold structures during
the molding process.

2.3.2 Fabrication

Injection molding was performed using the BOY 22M-A precision injection molding
machine (BOY Machines Inc., Exton, PA) shown in Figure 2.8 [74, 78]. The nanostructured
mold was inserted into the custom-designed removable molding block and loaded into the
injection molding machine. Cyclic olefin copolymer (COC) thermoplastic resin (Zeonor 1060R, \( T_g = 100 \, ^\circ C \)) was purchased from Zeon Chemicals (Louisville, KY) and loaded into the hopper in pellet form. The COC pellets were dried in nitrogen flow for 1 hour before injection molding. Table 2.2 shows the optimized conditions used for nanoinjection molding. The mold temperature, which was controlled by an oil heater, was maintained at 112 °C. The injection pressure was set to 19,000 psi, and the polymer flow rate was 40 ccm/s. After injection into the mold cavity, the polymer was allowed to cool for 1 minute before being removed by automated ejector pins.
Figure 2.8. Photograph of the BOY 22M-A injection molding system at the University of Cincinnati.

Table 2.2. Nanoinjection molding conditions for BOY 22M-A.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Mold Temp.</td>
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<td>Polymer Flow Rate</td>
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</tr>
<tr>
<td>Injection Pressure</td>
<td>19,000 psi</td>
</tr>
</tbody>
</table>

2.4 Experimental Results

A major requirement for the nano-scale mold is a planar and smooth surface on which nanostructures are patterned. To determine the surface condition of the mold, the Ni disk was inspected during the lapping/polishing procedure. Figure 2.9 shows optical micrographs of the Ni
surface after (a) lapping and (b) final polishing step. The desired mirror-finish Ni surface was achieved after the polishing step was completed. The surface roughness of the Ni disk was studied by surface profilometry (KLA-Tencor P10 Profilometer) to determine the contrast between the background roughness and the fabricated nanostructures. Scans of the mold were completed with the following parameters: 100 µm scan length, 2 µm/s scan speed, 200 Hz sampling rate, 1 mg stylus force, and 65 µm/0.04 Å resolution. The measured surface roughness for the nanomold was 8 ± 1 nm, indicating a suitable surface for producing nano-scale mold structures.

Figure 2.9. Optical micrographs of Ni mold disk surface after (a) lapping and (b) polishing. Scale bars = 30 µm.

After pre-conditioning the Ni mold disk by lapping and polishing, nanostructures were fabricated on the Ni substrate by EBL and liftoff metallization with Ni or Ti. Using the fabrication methods described previously, structures were fabricated across a range of widths from 10 µm down to 100 nm, with heights ranging from 100 nm to 350 nm. After fabrication was complete, the nanomold structures were inspected using scanning electron microscopy (SEM, Raith 150) at 10 kV accelerating voltage. Figure 2.10 shows the results for 300 nm wide Ni/Ni nanomold structures in both 1D (lines) and 2D formats (squares).
Figure 2.10. Results from nanomold fabrication: (a) SEM image of 300 nm 1D nanostructures on Ni surface; (b) higher magnification SEM image of 1D mold structure; (c) SEM image of 300 nm 2D nanostructures on Ni surface; (d) higher magnification SEM image of 2D mold structure.

After the mold fabrication was complete, the Ni disk was used for injection molding of COC to create polymer templates using the previously described fabrication method. To verify the successful replication of mold structures in the polymer, templates were collected from the injection molder and inspected via SEM. Since SEM imaging requires a conductive surface to
avoid charging effects, the polymer templates were coated with a thin gold (Au) film by sputter deposition. Sputtering was performed (Denton II Cold Sputter/Etch Unit, Denton Vacuum) at 25 mA for 120 seconds to achieve a thin conductive gold film for SEM imaging. The polymer templates were inspected with SEM (Raith 150) and the results shown in Figure 2.11. Template patterns were observed with shapes corresponding to the shape of the mold structures, thus ridges and posts on the mold resulted in trenches and pores, respectively, on the polymer surface.
Figure 2.11. Results from nanoinjection molding: SEM images of (a) array of 300 nm wide 1D template patterns; (b) higher magnification view of a single trench; (c) array of 300 nm wide 2D template patterns; (d) higher magnification view of a single pore.

The surface roughness of the COC templates fabricated by nanoinjection molding was studied by surface profilometry (KLA-Tencor P10 Profilometer) to determine the contrast between the background roughness and the fabricated nanostructures. Scans of the polymer were completed with the following parameters: 100 µm scan length, 2 µm/s scan speed, 200 Hz
sampling rate, 1 mg stylus force, and 65 µm/0.04 Å resolution. The measured surface roughness for the polymer template was 12 ± 4 nm, indicating a suitable background for distinguishing the replicated patterns.

The fidelity of pattern transfer from the nanomold to the polymer template was studied to determine the accuracy of the nanoinjection molding process. SEM analysis was used to measure the width of the mold structures and their corresponding feature size in the polymer template. The results from SEM analysis of pattern transfer are shown in Table 2.3. Close agreement between mold structures and polymer template patterns were observed over the range from 300 nm to 5 µm, indicating nano-scale precision is possible with the developed nanoinjection molding process.

Table 2.3. Fidelity of pattern transfer from mold structures to polymer template patterns.

<table>
<thead>
<tr>
<th>Mold</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>288 ± 3 nm</td>
<td>289 ± 2 nm</td>
</tr>
<tr>
<td>394 ± 5 nm</td>
<td>391 ± 2 nm</td>
</tr>
<tr>
<td>550 ± 2 nm</td>
<td>548 ± 5 nm</td>
</tr>
<tr>
<td>680 ± 5 nm</td>
<td>673 ± 6 nm</td>
</tr>
<tr>
<td>1349 ± 22 nm</td>
<td>1308 ± 8 nm</td>
</tr>
<tr>
<td>5347 ± 47 nm</td>
<td>5355 ± 40 nm</td>
</tr>
</tbody>
</table>
The pattern transfer from the height of the mold structures to the depth of the polymer template patterns was also studied. Mold structures of varying heights (100 nm and 200 nm) were prepared and used for injection molding using the previously described techniques. After completion of injection molding, atomic force microscopy (AFM, NanoSurf Easy Scan) was used in non-contact mode to measure the depth of the resulting polymer template patterns. The results from AFM analysis are shown in Figure 2.12. The measured depths of 55 nm and 80 nm correspond to mold patterns of 100 nm and 200 nm in height, respectively. The difference between the height of the mold pattern and the depth of the polymer template patterns is likely the result of insufficient filling of the mold patterns during the injection molding process.

![Figure 2.12. Results from nanoinjection molding: AFM surface images of (a) an array of 55 nm deep pores; (b) an array of 80 nm deep pores.](image)

In order for nanoinjection molding to be considered a mass-producible fabrication technique, the mold must be used for several tens to hundreds of injection molding cycles for the
production of polymer templates. As a result, the lifetime of mold structures is a critical aspect of this fabrication approach. To test the durability of the mold, a set of test patterns was fabricated on the mold and used to quantify the failure and success rate of mold structures as a function of feature size and number of injection molding cycles. Arrays of rectangular shaped patterns were designed with feature sizes ranging from 200 nm to 5 μm (width) and lengths of 65 μm. After mold fabrication was complete, the structures were replicated by nanoinjection molding with COC using the previously described technique. Polymer templates were collected from injection molding after 1, 50, 100, 150, and 200 cycles. The templates were inspected with optical microscopy to determine the number of mold structures remaining as a percentage of the original number of mold structures prior to injection molding. The results are shown in Table 2.4.
Table 2.4. Number of remaining mold structures (displayed as percentage of original number of mold structures) as a function of feature size and number of injection molding cycles.

<table>
<thead>
<tr>
<th>Feature Size</th>
<th>Number of Injection Molding Cycles</th>
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<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>200 nm</td>
<td>62%</td>
</tr>
<tr>
<td>300 nm</td>
<td>99%</td>
</tr>
<tr>
<td>400 nm</td>
<td>100</td>
</tr>
<tr>
<td>500 nm</td>
<td>100%</td>
</tr>
<tr>
<td>1 μm</td>
<td>100%</td>
</tr>
<tr>
<td>2 μm</td>
<td>100%</td>
</tr>
<tr>
<td>5 μm</td>
<td>100%</td>
</tr>
<tr>
<td>10 μm</td>
<td>100%</td>
</tr>
</tbody>
</table>

For 200 nm mold patterns, significant degradation occurred after the first cycle, and less than 35% of structures remained after 50 cycles. For mold patterns with features in the range between 300 nm – 1 μm, more than 95% of structures remained for each feature size, even after 200 injection cycles. For patterns larger than 1 μm, significant degradation was observed after 100 injection cycles, in which less than 90% of structures remained for each feature size. These
results indicate the nanoinjection molding method described in this work is suitable for mass-production of structures ranging from 300 nm – 1 µm in feature size (width).

2.5 Conclusions

In this section, a new approach to fabricating templates for nano-assembly using nanoinjection molding was presented. The development of nano-scale mold structures on a replaceable Ni mold disk was described and results were given for production of 1D and 2D mold structures. The mold patterns were used for successful replication of polymer templates using injection molding with cyclic olefin copolymers (COC). The fidelity of pattern transfer from the mold structures to the polymer templates was studied, showing excellent reproducibility in the range of 300 nm – 1 µm. Additionally, the durability of the mold structures was studied as a function of feature size and number of injection molding cycles. Mold features in the range of 300 nm – 1 µm were shown to be durable for 200 injection cycles, indicating the suitability of this approach for mass-production of nano-scale features in polymer templates.
CHAPTER 3

NANOPARTICLE ASSEMBLIES ON POLYMER NANOTEMPLATES
3.1 Introduction

The development of nanoparticle assemblies on solid substrates is important for a variety of emerging applications, including electronic, photonic, and biosensing devices [10, 11]. As a result of the improved performance offered for these applications, there is a strong desire for the development of nanoparticle assemblies for commercial applications, which will require mass-producible and low-cost fabrication techniques. As explained in Chapter 1, a number of different techniques have been developed for the assembly of nanoparticles on solid substrates, including direct manipulation [53] and solution-based methods [54]. One approach that has seen significant application is the use of a patterned substrate as a template for the capillary-driven assembly of nanoparticles [58, 64, 66]. Despite promising early results, this methodology is not easily scaled for mass-production settings due to the lack of an appropriate fabrication method for the templates, which should be manufactured at high-throughput levels while maintaining low costs and nano-scale resolution. Previously, templates for nanoparticle assembly have been fabricated using diblock copolymers [64], optical lithography [65], interference lithography, [60], electron beam lithography [66], and nanoimprint lithography [50]. However, none of these approaches provides high-throughput fabrication of nano-scale template patterns with control over pattern shapes. Additionally, the use of capillary force to selectively assemble nanoparticles in template patterns involves a complex interaction between the capillary force and surface charges on the nanoparticle and template surface [58], which limits its widespread implementation as a general assembly technique.

To enable the development of mass-producible nanoparticle assemblies, new methods are needed for both the fabrication of templates and their subsequent use for the assembly of
nanoparticles. As described in Chapter 2, injection molding is a high-throughput, low-cost technique that can be used to create polymer structures with nanometer resolution. If the polymer templates produced by nanoinjection molding can be used for the assembly of nanoparticles, mass-producible nanoparticle-based devices may be envisioned. Additionally, a new technique is sought for the assembly of nanoparticles that does not rely on a complex use of surface charges and capillary forces to provide selective assembly, thus greatly simplifying the assembly process.

3.2 Assembly Method

To develop a new method for assembling nanoparticles on polymer templates, the standard template-assisted self assembly (TASA) approach was first reviewed. TASA is a popular approach to nanoparticle assembly involving the use of a patterned substrate that guides the assembly of nanoparticles through a combination of capillary force and template dimensions [58]. In this approach, a solution containing particles is flowed over a patterned template. As the solution is removed from the template, the receding meniscus causes a capillary force to be exerted on the particles, causing them to become trapped in the relief patterns on the template surface. Additionally, the capillary force also causes particles that are not trapped in template patterns to be pushed across the template surface away from the relief patterns, thus allowing for assembly only in the patterned areas. A critical aspect of this technique is the role of surface charges on the nanoparticle and template surfaces [58]. In general, a slightly repulsive interaction is desired so as to avoid having particles randomly attaching to the template surface outside the pattern areas. However, if the repulsive force between the nanoparticle and the template surface is too large, the nanoparticle will be repelled away from the surface, thus preventing successful assembly in the recessed pattern areas. On the other hand, an attractive force between the
template and the nanoparticle will result in uniform deposition without selectivity in the recessed pattern areas. As a result, a finely tuned process is required involving the nanoparticle surface charge, template surface charge, solution pH, rate of template withdrawal, rate of solvent evaporation, etc., which increases the complexity of the fabrication technique [64]. Another factor that must be taken into account for particles below 1 µm is the effect of Brownian motion, which is the irregular and random motion due to collisions with gas and liquid molecules. The equation for diffusion by Brownian mechanisms is given as

\[ D = \frac{C_c kT}{3\pi\mu D_p} \]  

(1)

where \( D \) is the diffusion coefficient, \( C_c \) is the Cunningham slip correction factor, \( k \) is the Boltzmann constant, \( T \) is the temperature, \( \mu \) is the viscosity of the fluid, and \( D_p \) is the particle diameter [82]. As shown in Equation 1, the effects of Brownian motion become more pronounced as the size of the nanoparticles used for assembly decreases, thus capillary force may no longer be effective at such scales in providing selective assembly of particles in template patterns [58, 83].

To overcome the limitations of the TASA approach, a new method was developed for the selective assembly of nanoparticles in template patterns. The new technique, which is shown in Figure 3.1, involves the deposition of nanoparticles on the template surface and their selective removal by a mechanical wiping process [78]. First, nanoparticles are deposited across the surface of a polymer template, which is fabricated by the nanoinjection molding method described in Chapter 2. The template surface contains relief patterns which are negative replicas of the original mold structures, thus ridges and posts on the mold become trenches and pores in the polymer template. After the nanoparticles have been uniformly deposited across the surface of the template, including inside the relief patterns, the surface of the template is mechanically
wiped. Nanoparticles attached to the template surface are thus removed during the wiping process, whereas particles in the template patterns are shielded from the wiping process and are retained. As a result, the deposition and wiping process provides selective assembly of nanoparticles in the template relief patterns.

Figure 3.1. Schematic diagram of nanoparticle assembly method: (a) deposition of nanoparticles on polymer surface by dip-coating technique; (b) selective removal of nanoparticles by wiping the template surface [78].

The proposed concept of nanoparticle assemblies on the polymer templates requires two major process steps: nanoparticle deposition and selective removal. The nanoparticles can be deposited on the polymer template surface in a variety of solution-based methods, including Langmuir-Blodgett, self-assembled monolayer (SAM), layer-by-layer, electrostatic deposition, and convective assembly [54]. Among these techniques, convective assembly has the most
potential because it is inexpensive, high-throughput, and can be used for creation of mono- or multilayer assemblies [54]. In the convective assembly approach, a solution containing nanoparticles is brought into contact with the substrate surface, which can be accomplished in two different ways. When a large volume of nanoparticle solution is available, a dip-coating technique may be used in which the template is immersed in a solution containing nanoparticles and slowly removed. When a small volume of solution is available, it may be more appropriate to deposit the nanoparticle solution directly onto the template via a pipette, which reduces the volume of solution needed to complete an assembly. In either case, the nanoparticles are deposited on the template surface by a convective assembly mechanism [84]. This mechanism is the result of convective flow that is stimulated by the evaporation of the solution containing the nanoparticles, which forces the particles toward the rear meniscus and three-phase contact line (gas, liquid, solid). When the thickness of the solvent becomes approximately equal to the particle diameter, the attractive capillary force between particles leads to the formation of a close-packed film of nanoparticles on the substrate surface [85, 86]. A critical aspect of this deposition technique is the wettability of the substrate surface, which should be hydrophilic (Figure 3.2a). If the surface condition is instead hydrophobic, the confinement effect of the meniscus is reduced and particles are simply pushed along the substrate surface instead of depositing as a film (Figure 3.2b) [86].
Figure 3.2. Effect of surface condition on convective assembly of nanoparticles by dip-coating technique showing: (a) assembly on hydrophilic (wettable) surface; (b) no assembly on hydrophobic (non-wettable) surface. Adapted from [86].

The wettability of a substrate surface is directly related to the surface free energy, which is expressed in Young’s equation as

$$\gamma_s = \gamma_l \cos(\theta) + \gamma_{sl}$$  \hspace{1cm} (2)

where $\theta$ is the contact angle of a liquid drop on the surface, $\gamma_s$ is the surface free energy of the solid, $\gamma_l$ is the surface free energy (surface tension) of the liquid, and $\gamma_{sl}$ is the interfacial free energy between the solid and the liquid [82]. Therefore, to create the appropriate hydrophilic surface condition for convective assembly, the surface energy should be increased by reducing the contact angle.

The second major component of the assembly process is the selective removal of particles. A number of different techniques have been developed for the removal of particles from surfaces, primarily as a necessity for removal of contamination in the semiconductor industry. Examples include blade cleaners, brushes, centrifuges, gas jets, high shear fluids, and
ultra- or megasonic techniques [87, 88]. The primary considerations for choosing the particle removal technique include the ability to provide sufficient force to displace a particle from its surface position, compatibility with the substrate so as to avoid damaging the surface, instrumentation requirements, process throughput, and cost. To meet the requirements for removing nanoparticles from the polymer surface while retaining particles in the template relief patterns, a simple wiping method was developed using a commercially available clean room wiper (TechniCloth II, ITW Texwipe). The wiper material (55% cellulose, 45% polyester) demonstrates high absorbency and low particulate contamination while also being softer than a blade, which could scratch and damage the polymer surface during wiping [89].

To determine whether the hand-driven wiping process provides sufficient force to remove nanoparticles from the polymer surface, the adhesive force between the nanoparticles and the polymer template was calculated. It has been postulated that the dominant adhesive force between particles and surfaces under ambient conditions is due to capillary force that arises from the water meniscus that exists between them [82, 90]. This meniscus forms as a result of condensation from the ambient humidity, and the associated surface tension leads to the exertion of a capillary force that holds the particle and surface together. A standard approximation of this capillary force can be made using the following equation

$$F_c = 4\pi R \gamma \cos \theta$$

where $\gamma$ is the solution surface tension, $R$ is the particle radius, and $\theta$ is the water-surface contact angle [90]. Substituting values for a 100 nm diameter nanoparticle on hydrophilic surface ($R = 50$ nm, $\gamma = 0.072$ N/m, $\theta = 40^\circ$) yields an adhesion force of 35 nN. To estimate the force generated by the wiping process, a simple model is used with the wiper and the template surface treated as planes with area $A$. Assuming a thin-film of lubricant (water) between the surfaces that
causes them to be separated by distance \( D \), the frictional force experienced by the surfaces is expressed as

\[
F = \frac{\eta Av}{D} \quad (4)
\]

where \( \eta \) is the fluid viscosity and \( v \) is the velocity at which the surfaces move past each other [91]. Substituting estimated values \( A = 1 \text{ cm}^2 \), \( \eta = 1 \text{ cP} \), \( v = 0.25 \text{ cm/s} \), and \( D = 1 \mu\text{m} \) yields a frictional force of 0.25 mN. For comparison, the average human exerts a force on the order of several N with their index finger without experiencing discomfort or fatigue [92]. Thus the wiping method is sufficient for generating the necessary force for nanoparticle removal.

### 3.3 Fabrication

Polymer templates were fabricated by nanoinjection molding with cyclic olefin copolymers (COC), as described in Chapter 2. Briefly, a master mold for injection molding was produced by electron beam lithography (Raith 150) and metallization with liftoff. The master mold was inserted into the removable molding block for the injection molding machine (BOY 22M-A) and used for injection molding of COC. After injection molding was complete, the polymer templates were cleaned by sequentially washing with acetone, methanol, and de-ionized (DI) water for 1 minute in an ultrasonic bath (Branson 3210) and then dried in nitrogen flow. Since the native condition of COC polymer is hydrophobic (measured contact angle of 96.8 °), the templates were treated by oxygen plasma to create a hydrophilic surface condition. The templates were placed in a reactive ion etcher (RIE, March CS-1701 or Technics Series 85) and treated with oxygen plasma at 20 sccm and 100 W for 60 s. After plasma treatment, the contact angle of the templates was re-measured. The resulting surface displayed a measured contact angle less than 40°, indicating hydrophilic surface condition.
Nanoparticle solutions were prepared from stock solutions obtained from commercial vendors. Colloidal silica (SiO$_2$) solution, 80 ± 2 nm particle diameter, 50% suspension in water, was obtained from Allied High Tech. Inc. (Rancho Dominguez, CA) and used as received. Colloidal SiO$_2$ solution (LUDOX TM-50), 22 nm particle diameter, 50 wt.% suspension in water, was purchased from Sigma-Aldrich (Milwaukee, WI) and used as received. Antimony (V) oxide (Sb$_2$O$_5$) colloidal solution, 55 ± 3 nm particle diameter, 30% dispersion in water, was obtained from Alfa Aesar (Ward Hill, MA) and used as received.

For the dip-coating technique, the polymer template was dipped in a beaker containing nanoparticle solution for 1 minute before removing and drying on a level surface at room temperature for 1 minute. For the pipette technique, 10 µL of nanoparticle solution was pipetted (VoluMate, Mettler Toledo) onto the template surface and allowed to dry on a level surface at room temperature for 1 minute. To remove nanoparticles from the polymer surface, commercially available clean room wipes (TechniCloth II, ITW Texwipe) were wetted with DI water and used to softly wipe the template surface [78].

3.4 Experimental Results

3.4.1 Different Nanoparticle Types and Sizes

After fabrication was complete, the templates were inspected by SEM to determine the outcome of the nanoparticle assembly process. Since SEM imaging requires a conductive surface to avoid charging effects, the polymer templates were coated with a thin Au film by sputter deposition (Denton II Cold Sputter/Etch Unit, Denton Vacuum) at 25 mA for 120 seconds. The nanoparticle assemblies were inspected with SEM (Raith 150, 10 kV) and the results shown in Figure 3.3. As expected, assemblies of SiO$_2$ and Sb$_2$O$_5$ nanoparticles were achieved in the
polymer template patterns. For each nanoparticle type and size, the nanoparticles were assembled in the template relief patterns and minimal contamination from residual nanoparticles remaining on the polymer surface was observed, indicating successful assembly. Additionally, the nanoparticle assemblies showed uniformity over large areas up to hundreds of square micrometers.

Many applications of the nanoparticle assemblies will require subsequent processing steps after assembly to create the final device. Therefore, it is highly desired that the nanoparticle assemblies be stable under normal microfabrication processing conditions. To test the stability of the nanoparticle assemblies, the assembled structures were subjected to standard clean room processing conditions. The nanoparticle-assembled templates were sequentially washed with DI water, acetone, methanol, and isopropyl alcohol. After washing, the templates were placed in an ultrasonic bath (Branson 3210) for 30 seconds. The nanoparticle assemblies were then inspected by optical microscopy. No distortion or degradation of the nanoparticle assemblies was observed as a result of the post-assembly procedures, indicating the suitability of the technique for fully integrated fabrication processes [78].
Figure 3.3. Results from nanoparticle assembly on the polymer template: SEM images of (a) 80 nm SiO$_2$ nanoparticles; (b) 55 nm Sb$_2$O$_5$ nanoparticles; and (c) 22 nm SiO$_2$ nanoparticles in arrays of 1D template patterns. Insets show higher magnification views (scale = 200 nm) [78].
3.4.2 Effect of Template Geometry

An important aspect of a nanoparticle assembly technique is its capacity for providing control over the assembled structures, such as the shape of the assembly and the quantity of nanoparticles in the assembly. In the newly developed method, the shape of the nanoparticle assembly is controlled by the template pattern, thus 1D template patterns (trenches) result in the 1D nanoparticle assemblies shown in Figure 3.3. To determine whether 2D nanoparticle assemblies could be fabricated with this technique, square-shaped template patterns produced by nanoinjection molding were used for assembly of 80 nm SiO$_2$, 55 nm Sb$_2$O$_5$, and 22 nm SiO$_2$ nanoparticles. After assembly was complete, the nanoparticle-assembled templates were inspected by SEM and the results shown in Figure 3.4. As expected, assembly of SiO$_2$ and Sb$_2$O$_5$ nanoparticles was achieved in 2D template patterns. For each nanoparticle type and size, the nanoparticles were assembled in the template patterns and minimal contamination was observed from residual nanoparticles remaining on the polymer surface. Additionally, uniformity was observed over large areas up to hundreds of square micrometers, as shown in Figure 3.5.
Figure 3.4 Results from nanoparticle assembly: SEM images showing (a) 80 nm SiO$_2$ nanoparticles; (b) 55 nm Sb$_2$O$_3$ nanoparticles; and (c) 22 nm SiO$_2$ nanoparticles in arrays of 2D template patterns. The insets show higher magnification views of the assemblies (scale bars = 200 nm).
For many applications, it will be important to control the number of nanoparticles assembled in a given structure. Since the template pattern determines the shape of the assembly, it follows that the size of the template pattern will influence the number of nanoparticles assembled in a structure. To test this hypothesis, 2D template patterns of varying width were fabricated and used for assembly of 80 nm SiO$_2$ nanoparticles. After assembly was complete, SEM imaging was used to quantify the number of nanoparticles captured in each pattern and the results shown in Figure 3.6. The measured results were compared with a predicted value in which nanoparticles are considered squares with 80 nm diameter and calculated for maximum coverage in the template pattern. The results show the template pattern dimensions can be used
to precisely control the number of nanoparticles in the assembly. As a result, design rules can be used to select the appropriate pattern dimension to achieve the assembly of the desired number of nanoparticles.

Figure 3.6. Relationship between template pattern width and number of 80 nm silica nanoparticles in 2D template patterns.

**3.4.3 Size-Selective Assembly**

Another important aspect of a nanoparticle assembly technique is its potential for controlling the type of nanoparticle that is assembled in a particular area. For example, one region of the substrate should be assembled with nanoparticle type A while another region
should have nanoparticle type B assembled. There are many approaches that may be used to accomplish this objective. One route is to dip part of the substrate in the solution containing nanoparticle type A, then dip another part of the template in solution containing nanoparticle type B, and so on. A manual approach such as this would be sufficient for millimeter-scale control over selective assembly, which is suitable for a wide range of applications of the nanoparticle assembly technique. For advanced applications, it will be necessary to assemble nanoparticles of type A in close proximity to nanoparticles of type B, thus a more precise method for selective assembly is required.

Another possible route is to expose particular regions of the substrate while protecting others, thus allowing the entire substrate to be dipped into nanoparticle solution. In such an approach, region 1 would be exposed while region 2 is protected as the substrate is dipped in solution containing nanoparticle type A. After assembly, the substrate would be re-patterned to protect region 1 while exposing region 2 for assembly of nanoparticle type B. Photolithography could be used to protect one region of the resist while another region is exposed, providing flexibility in patterning. However, this approach would require multiple photolithography steps, which adds to the complexity of the assembly process and lowers the overall throughput of the fabrication technique.

A preferable solution for selective assembly would involve the assembly of different nanoparticle types in different regions of the substrate without adding additional patterning steps. A possible solution to this requirement is the use of size-selective assembly, in which assembly selectivity is achieved through a combination of the template pattern dimensions and the size of the nanoparticle to be assembled. For instance, if the diameter of the nanoparticle is larger than the width of the template pattern, the nanoparticle will not be able to be deposited inside that
pattern. Likewise, if the nanoparticle diameter is larger than the depth of a template pattern, some surface area of the nanoparticle will be exposed above the template surface and thus the particle will be removed during the mechanical wiping process. On the other hand, if the nanoparticle diameter is smaller than the width and depth of the template pattern, that nanoparticle would be maintained in the template pattern after completion of the mechanical wiping process. Thus, size selectivity could be realized by varying the template pattern depth in specific regions on the polymer surface.

To test this hypothesis, template patterns with varying depths (80 nm and 55 nm) were fabricated and used for assembly of two nanoparticles with different diameters (80 nm SiO$_2$ and 55 nm Sb$_2$O$_5$). The results of the experiment are shown in Figure 3.7. For the 55 nm Sb$_2$O$_5$ nanoparticles, assembly was achieved in both 80 nm and 55 nm deep template patterns. These results are expected since the nanoparticle diameter is approximately equal to or smaller than the template pattern depth in both cases. For the 80 nm SiO$_2$ nanoparticles, assembly was achieved in the 80 nm deep patterns, but not in the 55 nm deep patterns. These results are also expected since the nanoparticle diameter was smaller than the template pattern depth in only one case and significantly larger than the template pattern depth in the other case.

The results indicate that template pattern dimensions can be used to control the size of a nanoparticle that is assembled in a particular region on the substrate surface. Additionally, since the different sized nanoparticles used in this experiment were also composed of different materials, the selectivity of the assembly process is also extended to provide control over the type of nanoparticle that is assembled in a particular region on the substrate surface.
Figure 3.7. SEM images and associated schematics showing size-selective assembly of nanoparticles using the polymer template pattern depth as selection criteria: (a) 80 nm silica nanoparticles in 80 nm deep pattern; (b) empty pattern resulting from 80 nm silica nanoparticles removed from 55 nm deep pattern during wiping; (c) 55 nm Sb$_2$O$_5$ nanoparticles in 80 nm deep pattern; (d) 55 nm Sb$_2$O$_5$ nanoparticles in 55 nm deep pattern. Scale bars = 200 nm.
3.5 Conclusions

In this section, a new approach to the assembly of nanoparticles on solid substrates was described and results presented. Polymer templates fabricated by nanoinjection molding were used for the assembly of nanoparticles. A new nanoparticle assembly technique was developed involving deposition of nanoparticles on a polymer template and their selective removal by a mechanical wiping process. Results were demonstrated for the assembly of multiple sizes and types of nanoparticles in both 1D and 2D template patterns. The dimensions of the template patterns were used to control the number, size, and type of nanoparticles in an assembly. Since the template fabrication method and subsequent assembly technique are both rapid, high-throughput processes, this approach may enable the mass-production of nanoparticle-based devices for commercial applications.
CHAPTER 4
NANOELECTRODES ON POLYMER
NANOTEMPLATES
4.1 Introduction

Nanoelectrodes have become important components for a range of devices, including electronics and biosensors [4, 22]. As described in Chapter 1, the reduction of electrode dimensions to the nano-scale allows increased integration density, thereby improving the functionality of electronic devices. Additionally, the increased performance offered by nanoelectrodes for specific applications, such as organic electronics and electrochemical biosensors, may lead to breakthroughs in flexible electronics [28, 93] and the detection of trace quantities of biomolecules [94], respectively.

As a result of the increased interest in nanoelectrodes and nanoelectrode arrays, there is a strong desire to develop devices for commercial applications, which will require mass-producible fabrication methods. Nanoelectrodes have been fabricated by a variety of techniques including electron beam lithography [43] and nanoimprint lithography [45], however neither of these techniques allow high-throughput fabrication required for mass-production settings. An approach that has shown promising results is the use of a pre-fabricated template that is combined with a metallization process for the creation of a nanoelectrode array [51]. In this methodology, a polymer substrate with pores that traverse the entire thickness of the material is coated with a gold (Au) film by electroless plating. During the plating process, all exposed areas of the porous membrane are coated with Au, thus Au is deposited on both the top and bottom surfaces of the polymer. Additionally, the pores become filled with Au and form nanowires that traverse the full-thickness of the polymer. After removal of either the top or bottom gold surface with adhesive tape, the tips of the gold nanowires that traverse the polymer membrane are revealed, forming an array of nanoelectrodes. While this method is a rapid, low-cost approach to the
fabrication of nanoelectrodes, it does not provide control over the electrode geometries, including the length, width, spacing, and number of electrodes in the array, which are determined by the pore dimensions of the polymer substrate.

To meet the requirements of nanoelectrodes for commercial applications, a new fabrication approach is needed that can generate nanoelectrodes at mass-production levels while maintaining low costs and preserving design flexibility for realization of specific electrode patterns. As described in Chapter 2, injection molding can be used for the production of polymer templates with control over nano-scale pattern shapes at production rates approaching 1 chip per minute. If polymer templates from nanoinjection molding can be combined with a suitable metallization technique for the patterning of electrodes, mass-producible nanoelectrode-based devices may be realized.

4.2 Patterning Technique

A new approach to nanoelectrode fabrication was developed in this work by using a variation on the patterning technique for nanoparticle assemblies, which was described in Chapter 3. As with the nanoparticle assembly method, the new nanoelectrode patterning technique involves the deposition and selective removal of a material, in this case a metal, by using the polymer template patterns created by nanoinjection molding [78]. As shown in Figure 4.1, the fabrication technique begins with the deposition of a metal on the surface of the polymer template. The deposited metal conforms to the surface profile of the template, thus preserving the relief profile provided by the template patterns. The surface of the polymer substrate is then mechanically wiped to remove all metal outside the template patterns, whereas metal in the relief patterns is retained to form planar nanoelectrodes just below the surface of the polymer template.
Figure 4.1. Schematic diagram of electrode patterning technique by metallization of polymer template with selective removal [78].

The method for depositing metal on the template surface is a primary concern for this newly developed technique. A number of different techniques are available for the deposition of metal on a substrate, including sputtering, evaporation, electroplating, and electroless plating [95]. Sputtering and evaporation have been used extensively to produce metal thin-films on a variety of substrates, but the adhesion between the substrate and the metal is too strong to allow selective removal of the residual metal by the proposed method. Electroplating has been broadly used for the deposition of a wide range of metals on substrates; however a conductive layer is required to provide the electrical potential to drive the reaction, thus it is not suitable for plating on non-conductive substrates such as plastics.
An attractive alternative for metalizing plastic substrates comes in the form of electroless plating. In electroless plating, a metallic thin-film is deposited as a result of a chemical reaction between metal ions and a reducing agent, which are both in solution, and a catalyst on the substrate surface [96]. When the metal ions come into contact with the catalyst in the presence of the reducing agent, the metal is reduced and deposited on the catalyst surface. Additionally, the metal to be deposited will continue to plate onto the previously deposited layers until the metal ions or reducing agent is removed, which is known as auto-catalysis. Electroless plating offers several benefits over traditional electroplating methods, including the potential for deposition on nonconductive substrates, uniform thickness of the plated film, and simple processing equipment and materials [96]. Additionally, a wide range of metals can be deposited by electroless plating techniques, including Ni [97], copper (Cu) [98], Ag [99], and Au [100-102]. Furthermore, the bond strength of films prepared by electroless plating, is typically less than those deposited by e-beam evaporation, thus the film should be easily removed by the previously developed wiping method [103, 104].

The mechanism for electroless plating can be described as follows. First, the reducing agent in solution is oxidized on the catalyst surface. The electrons released from this reaction are then transferred to the metal ions in solution, which are reduced and deposited on the catalyst. Thus the plating process involves two synchronous electrochemical reactions in which electrons serve as an active intermediate product [96]. The reactions can be described by the following equations

\[ \text{Red(aq)} \rightarrow \text{Ox(aq)} + \text{me}^- \]  \hspace{1cm} (1)

\[ \text{M}^{n+}(aq) + \text{ne}^- \rightarrow \text{M(s)} \]  \hspace{1cm} (2)
where Red is the reducing agent, Ox is the oxidized form of the reducing agent, M is the metal, and e is electrons [105].

To accomplish the electroless plating of metal on the polymer templates, the polymer surface must first be activated with a catalyst [106]. A number of catalysts have been reported in the literature, including palladium (Pd) [95], Ag [51, 107], and Au [108, 109]. Au was selected as the catalyst material for this work due to its stability and its ease of processing by sputtering. The remaining requirements for electroless plating are metal ions and reducing agent in solution, which are selected for the specific metal to be deposited. Two commonly used metals were selected for the fabrication of nanoelectrodes in this work. Silver was chosen due to its excellent conductivity and lower cost compared to other metals, which makes it attractive for low-cost electronics applications [110]. Gold was selected due to its inertness and wide application as an electrode material for electrochemical sensors [34, 111].

For electroless deposition of metallic silver, a commercially available silver plating kit (SE100, Sigma-Aldrich) was purchased and used as received [112]. The kit contains two solutions: silver salt (AgNO$_3$) and reducing agent (hydroquinone) [112]. For electroless deposition of metallic gold, no commercial plating system was available, so the source of metal ions and reducing agent were purchased separately. There are two main approaches described in the literature for electroless plating of gold. One method utilizes Na$_3$Au(SO$_3$)$_2$ as the gold source and formaldehyde as the reducing agent [113, 114]. The second method involves gold chloride (HAuCl$_4$) as the gold source and hydroxylamine (NH$_2$OH) as the reducing agent [101, 108, 115-117]. The HAuCl$_4$/NH$_2$OH combination was selected due to its faster processing time, which is critical for the realization of a mass-producible fabrication approach [101]. Thus, the chemical reaction for electroless plating of gold can be described as
\[ \text{NH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + 4e^- + 4\text{H}^+ \]  

with a simultaneous reduction of Au(I) to Au(0) [101]. Gold chloride (HAuCl_4, HT104, Sigma-Aldrich) was purchased and a solution containing hydroxylamine hydrochloride (NH_2OH•HCl, 10% w/v, Aqua Solutions) was purchased for use as metal ion source and reducing agent, respectively.

4.3 Fabrication

Polymer templates were fabricated by nanoinjection molding with cyclic olefin copolymers (COC), as described in Chapter 2. Briefly, a master mold for injection molding was produced by electron beam lithography (Raith 150) and metallization with liftoff. The master mold was inserted into the removable molding block for the injection molding machine (BOY 22M-A) and used for injection molding with COC. After injection molding was complete, the COC templates were cleaned and activated for electroless plating. The polymer templates were cleaned by sequentially washing with acetone, methanol, and de-ionized water for 1 minute in ultrasonic bath (Branson 3210) and then dried in nitrogen flow. A thin, non-conducting layer of Au was deposited by sputter deposition (Denton II Cold Sputter/Etch Unit, Denton Vacuum) at 10 mA for 10 seconds to serve as the catalyst for electroless plating [78].

The catalyst-activated polymer templates were then used as substrates for electroless deposition of metal. For the electroless deposition of silver, 10 µL solutions of silver salt and reducing agent (SE100, Sigma-Aldrich) were mixed and pipetted onto the template surface for 1 minute. After rinsing in DI water, the template surface was softly wiped with clean room wipes (TechniCloth II, ITW Texwipe), which had been wetted with DI water, to remove residual Ag on the surface. This process was repeated until the desired metal thickness had been achieved [78].
For the electroless deposition of gold, the reducing agent (NH₂OH•HCl, 10% w/v, Aqua Solutions) was diluted by a factor of 10 through the addition of DI water. 10 µL solutions of the diluted reducing agent and the gold source (HAuCl₄, HT104, Sigma-Aldrich) were mixed and pipetted onto the polymer surface for 1 minute. After rinsing with de-ionized water, the template was softly wiped with clean room wipes, which had been wetted de-ionized water, to remove the residual Au on the surface. This process was repeated until the desired metal thickness had been achieved.

4.4 Experimental Results

Prior to its use in the newly developed method for the fabrication of nanoelectrodes, the electroless plating process was characterized for deposition of both Ag and Au films on catalyst-activated COC. Standard photolithography procedures were used to create resist patterns on a flat COC substrate, which had been activated by Au sputtering. Photoresist (Shipley S1818) was spin-coated on the template at 500 RPM for 10 seconds and 3000 RPM for 45 seconds, then soft-baked at 90 °C for 20 minutes. The resist was exposed using optical lithography (MJB3, Karl Suss) and developed in 1:4 solution of Microposit 351 and DI water. Electroless plating was performed on the patterned substrate for controlled time intervals and the residual photoresist was removed by liftoff in acetone. Following completion of the plating process, the thicknesses of the plated films were measured by profilometry (KLA-Tencor P10 Profilometer). The resulting plating rates for Ag and Au are shown in Figure 4.2. Linear growth of both Ag and Au films was observed for thicknesses approaching 100 nm. The linear growth profile indicates the plating time can be used as a control point for determining the final thickness of the metal film.
Since this thickness determines the height of the electrode in the template pattern, the plating time can be used to control the final thickness of the fabricated electrodes.

![Graph](image)

Figure 4.2. Thickness of metal film deposited by electroless plating as a function of plating time for Ag and Au on catalyst-activated COC.

To verify the utility of the electrode patterning technique for producing a range of electrode dimensions, templates containing 1D patterns (trenches) with dimensions ranging from 300 nm – 1 µm were used for the fabrication of Ag electrodes. After electroless deposition and patterning using the methods described previously, the polymer templates were visually inspected using optical microscopy and scanning electron microscopy (SEM, Raith 150). For SEM analysis, the templates were coated by Au sputter (Denton II Cold Sputter/Etch Unit, Denton Vacuum) at 25 mA for 120 seconds, which was required to prevent charging during
imaging. The results from fabrication of silver electrodes on the polymer nanotemplate are shown in Figure 4.3. Continuous Ag patterns were observed in the template patterns with no surface contamination from residual Ag on the polymer template surface. The Ag patterns displayed varying width from 1 µm - 375 nm and minimum spacing as small as 800 nm, indicating that precise control over electrode dimensions was facilitated by the width of the polymer template. Additionally, uniform patterning was observed over large areas up to hundreds of square micrometers. No disconnected electrodes (no open circuits) were observed in the fabricated electrode arrays, and adjacent electrodes were observed to be isolated from each other (no short circuits) [78].
Figure 4.3. Results from fabrication of silver electrodes: SEM images of (a) 1 µm wide electrodes; (b) 550 nm wide electrodes; (c) 460 nm wide electrodes; (d) 375 nm wide electrodes. Insets show higher magnification view of individual electrodes (scale bars = 300 nm) [78].

Templates containing 1D patterns were also used for the fabrication of Au electrodes. After electroless deposition and patterning using the methods described previously, the polymer templates were visually inspected using optical microscopy and scanning electron microscopy (SEM, Raith 150). The results from fabrication are shown in Figure 4.4. Metal patterns of
varying width from 1 µm – 600 nm were fabricated in array format. Similar to the results obtained for metallic silver, uniform patterning was observed for gold over large areas up to hundreds of square micrometers. No disconnected structures were observed in the fabricated arrays, and adjacent metal patterns were observed to be isolated from each other.

Figure 4.4. Results from fabrication of gold electrodes: SEM images of (a) array of 1 µm electrodes; (b) array of 600 nm electrodes. Insets show high magnification SEM images of the arrays (scale bars = 300 nm).

In order to use the metal patterns as electrodes, the fabricated structures must be electrically conductive and isolated from each other. To characterize the electrical performance of the Ag and Au electrodes, electrical connections were made to arrays of nanoelectrodes. Standard photolithography and liftoff processes were used to create contacts, traces, and pads to allow for measurements. The current-voltage (I-V) relationship for each metal was studied and the results displayed in Figure 4.5, showing linear relationships for both Ag and Au electrodes. A second experiment was conducted to verify that individual electrodes in the array were
electrically isolated from each other. Ag and Au nanoelectrodes were fabricated in an interdigitated array (IDA) format, thus allowing adjacent electrodes to be probed. Resistances greater than 30 MΩ were measured between the adjacent electrodes, indicating no short circuits were present in the arrays. The resistivity of the gold electrodes was experimentally measured for comparison with that of bulk gold. A 2 µm wide x 20 µm long gold electrode was fabricated by the described techniques and its resistance measured. The following equation was used to determine the resistivity of the electroless gold

\[ \rho = R \frac{A}{l} \]  

where \( \rho \) is the resistivity, \( A \) is the cross-sectional electrode area, and \( l \) is the electrode length [118]. The measured resistance of 13 Ω translates to a resistivity of 6.5x10^{-8} Ω-m, which compares well with the standard Au resistivity of 2.3x10^{-8} Ω-m [118].
Figure 4.5. Current-voltage (I-V) relationship for silver and gold nanoelectrodes fabricated by electroless plating and selective removal on the polymer template.

The results for electrode fabrication shown in Figures 4.3 and 4.4 demonstrate the utility of the new fabrication technique for producing electrodes with dimensions below 1 µm. For many applications, metal patterns of larger dimensions from 1 µm – 100 µm will be required for electrical interconnects, traces, and pads for interfacing with the outside world. Thus it was important to determine the upper limit of electrode dimensions that can be produced using this technique. To test the upper limit of the electrode fabrication technique, template patterns were produced with dimensions (width) of 10 µm, 5 µm, 2 µm, and 1 µm. The template patterns were used for the patterning of gold electrodes using the previously described techniques and the results shown in Figure 4.6. As expected, 1 µm template patterns were successfully used for the
patterning of electrodes. The 2 µm template patterns were also successfully used for patterning of electrodes, however, the 5 µm and 10 µm patterns resulted in unsuccessful patterning. The results indicate the failure at 5 µm and 10 µm feature size was the result of unwanted removal of metal from the template patterns during wiping. To verify this result, optical microscopy was performed to investigate the surface of the clean room wipers used for selective removal of metal from the polymer template surface. The results from microscopy showed the wiper surface was composed of thread-like fibers with minimum features measuring approximately 10 µm in diameter. It is concluded that template patterns with feature sizes in the 5-10 µm range and larger fail as a result of fibers physically fitting inside the template pattern and thus removing the metal during wiping. Therefore, the upper limit of the electrode fabrication technique is approximately 2 µm. If patterns of larger feature sizes are required for a specific application, the newly developed technique should be used in combination with a standard photolithography approach.
Figure 4.6. Results showing upper limit of fabrication process: optical micrographs of (a) 10 µm trench; (b) 5 µm trench; (c) 2 µm trench; (d) 1 µm trench. Scale bars = 10 µm.

For many applications, it will be necessary to pattern arrays of electrodes over large areas with minimal background contamination from residual plated metal on the surface of the polymer template. Thus, the fabrication approach must simultaneously provide nano-scale resolution over micro- and milli-scale areas. To demonstrate the utility of the new technique for such an approach, multiple arrays of template patterns were produced and used for patterning of gold electrodes in a simultaneous, parallel fabrication step. The results are shown in Figure 4.7. Successful fabrication of electrode arrays was achieved on the template surface at length scales approaching 1 mm.
Figure 4.7. Large area patterning of electrodes: (a) optical micrograph of COC template patterns before electrode patterning; (b) optical micrograph of electrode arrays after electrode patterning.

It is important to know the surface roughness of electrodes fabricated by this technique to determine their suitability for applications that require either rough or smooth electrode surfaces. To determine the roughness of the nanoelectrodes, the surface roughness of gold films created by electroless plating were measured with surface profilometry (KLA-Tencor P10 Profilometer). Electroless plating was performed on catalyst-activated COC for 3 minutes and the films were scanned using the following parameters: 100 µm scan length, 2 µm/s scan speed, 200 Hz sampling rate, 1 mg stylus force, and 65 µm/0.04 Å resolution. The measured surface roughness for the gold films was 4 ± 1 nm.

As mentioned earlier, an important aspect of the electroless plating process is its ability to deposit a thin-film on the template surface that can be later removed by the selective wiping process. While the major requirement for this approach is a relatively weak adhesive force
between the film and the surface so as to facilitate the removal of residual metal, the adhesion force should be strong enough that the patterned electrodes are mechanically stable. For example, after the electrodes have been fabricated, they may be exposed to cleaning solutions or prepared for further micro- and nanofabrication processes. To test the adhesion of the deposited gold film to the template, the standard “Scotch® tape” qualitative test was used [101, 103, 119]. Gold was deposited on catalyst-activated COC by electroless plating for 3 minutes and the template was rinsed with DI water and dried in nitrogen flow. The template was maintained at room temperature overnight and then tested for adhesion. Adhesive tape (Scotch Magic Tape, 3M) was applied to the template surface for 5 sec before slowly removing. Following removal of the adhesive tape, the gold film was inspected with optical microscopy. No removal of the plated film was observed. To determine the mechanical stability of the fabricated electrodes during post-processing, templates containing patterned electrodes were subjected to standard microfabrication processing conditions, such as rinsing with acetone, methanol, and DI water. The templates were then inspected with optical microscopy and SEM. No degradation of the electrode patterns was observed, indicating the compatibility of the electrodes with microfabrication processes.

4.5 Conclusions

In conclusion, this work has demonstrated a new approach to fabricating nanoelectrodes on polymer substrates. Nanoinjection molding with cyclic olefin copolymers was used to fabricate polymer templates. Deposition and selective removal of metal films using electroless plating was used to achieve Ag and Au patterns on the polymer templates. Electrodes with feature sizes ranging from 375 nm – 1 µm were demonstrated in array format over areas up to
hundreds of square micrometers. The electrodes were shown to be conductive and electrically isolated with linear I-V characteristic. The upper limit of the electrodes produced with this fabrication process was determined to be 2 µm and electrode arrays were demonstrated without contamination over lengths scales approaching 1 mm.
CHAPTER 5
ELECTROCHEMICAL NANOBIOSENSOR USING NANO INTERDIGITATED ARRAY
5.1 Introduction

As discussed in Chapter 1, there is a significant need for the development of ultra-sensitive biosensors as part of fully integrated lab-on-a-chip systems. The major requirements for these sensors include the capacity for trace detection of biomolecules while maintaining low-cost fabrication and potential for integration with lab-on-a-chip technologies, such as microchannels. A popular approach for biosensors involves electrochemical sensors, which are attractive for lab-on-a-chip applications due to their simple instrumentation requirements [33]. In particular, the use of microelectrodes in interdigitated array (IDA) format has received considerable attention as a result of their current enhancement property [34-36, 94, 120-126], which enables lower concentrations of species to be detected. The current generated at IDA electrodes can be described as

\[
I_{\text{lim}} = m b n F C_{\text{spe}} D [0.637 \ln \left( \frac{2.55(w + g)}{g} \right) - 0.19 \left( \frac{g}{w + g} \right)^2 ] \tag{1}
\]

where \( m \) is the number of electrode fingers, \( b \) is the electrode finger length, \( n \) is the number of electrons involved in the reaction, \( F \) is Faraday’s constant, \( C_{\text{spe}} \) is the concentration of the redox species, \( D \) is the diffusion coefficient of the redox species, \( w \) is the width of the electrode fingers, and \( g \) is the gap between the electrode fingers [37, 38].

There are several options available for increasing the current generated by an IDA electrochemical sensor, thus allowing the detection of lower concentrations of electrochemical species. An increase in the number of electrode fingers while maintaining electrode dimensions will result in higher limiting current. However, this increase in the overall size of the sensor is not desirable due to the limited space available on the lab-on-a-chip. Likewise, an increase in the finger length will result in higher current, but this approach also is unsuitable for lab-on-a-chip biosensors due to the increased sensor footprint. An alternative approach is to decrease the
spacing between the IDA electrodes to the nano-scale so as to increase the redox efficiency and therefore improve the limiting current and detection limit. Unfortunately, the ability to produce arrays of electrodes with reduced dimensions is limited by the IDA fabrication method, which is typically accomplished by photolithographic methods. Improved resolution can be obtained with electron beam lithography, however this is an expensive and low-throughput approach that is not suitable for mass-production of sensors for integration with lab-on-a-chips. On the other hand, the electrode patterning technique described in Chapter 4 has been demonstrated for high-throughput production of electrode arrays with nano-scale gaps. In this chapter, the development of an electrochemical nanobiosensor using the new electrode fabrication technique is discussed.

5.2 Design and Fabrication

As described in Chapter 1, a significant development in the field of electrochemical sensors arrived in the form of the interdigitated array (IDA) [35]. In this method, shown in Figure 5.1, two interdigitated electrodes are used as the anode and cathode, respectively, for the detection of a species that is electrochemically active. Voltages are applied to the electrodes such that the anode is maintained at the oxidation potential of the target species and the cathode is held at the reduction potential of the target species. When the oxidized form of the target species in solution comes into contact with the cathode, it is reduced according to the reaction

$$O + ne \rightarrow R$$  \hspace{1cm} (2)

where $O$ is the oxidized form of the target species and $R$ is the reduced form of the target species [94]. Likewise, when the reduced form of the target species comes into contact with the anode, it is oxidized according to the reaction

$$R \rightarrow O + ne$$  \hspace{1cm} (3).
As the reaction proceeds, the target species diffuses back and forth between the anode and the cathode, where it is cyclically reduced and oxidized [127]. This process, known as redox cycling [36], allows electrons to be exchanged between the electrodes, which generates a current that is proportional to the concentration of species in solution and the electrode geometry (Equation 1).

Figure 5.1. Schematic diagram showing principle of detection of redox species at IDA electrodes. Adapted from [38].

IDA electrodes have been applied for the detection of redox species in support of a range of applications. In many cases, IDA electrodes are used for the direct detection of redox species, such as dopamine [128], vitamin K [121], and Ru(NH$_3$)$_6^{3+}$ [127], which provides the benefit of directly detecting the target species in solution. Another major sensing application of IDA electrodes is the detection of a redox byproduct from another reaction involving a species that is not electrochemically active. For example, a target antigen needs to be detected, but it is not electrochemically active and thus cannot be directly detected at IDA electrodes. Instead, the target antigen can be captured in a sandwich immunoassay involving an enzyme label. The
enzyme label can then generate an electrochemically reversible product, which is then detected at
the IDA electrodes. Kim and coworkers demonstrated such a system using β-galactosidase as the
enzyme label, which produces p-Aminophenol (PAP) from 4-aminophenyl β-D-
galactopyranoside (PAPG) [120]. PAP is an electrochemically reversible species that is oxidized
to form 4-quinone imine (PQI) [120, 126], thus PAP and PQI form the redox couple that is
detected at the IDA electrodes (Figure 5.2). A major benefit of this approach is its flexibility for
detection of a wide range of target analytes, which is accomplished by changing the sandwich
immunoassay parameters, while physically detecting the same PAP-PQI redox couple.
Additionally, PAP demonstrates outstanding electrochemical properties, including low oxidation
potential and minimal electrode fouling [123]. As a result, PAP-PQI serves as an excellent model
redox couple for evaluating the performance of IDA sensors.

Figure 5.2. Schematic diagram showing redox cycling of p-aminophenol (PAP) and 4-quinone
imine (PQI) at IDA electrodes. Adapted from [38, 94, 126]
There are two major electroanalysis techniques used for the detection of redox species at IDA electrodes: cyclic voltammetry and chronoamperometry [129]. In the cyclic voltammetry method, one of the IDA electrodes is biased at a preset potential (reduction or oxidation) and the other electrode has a scanning potential applied. As the scanning potential approaches the redox potential, the current generated at the electrodes increases until a steady-state current is generated. This steady-state current is independent of potential and is proportional to the species concentration. A disadvantage of this approach involves the parasitic capacitance that arises at the scanning electrode due to the double layer at the interface between the solution and the electrode surface. As a result, the current generated at the scanned electrode involves a parasitic current (noise current), which negatively impacts the detection of redox species. The second electroanalysis technique, chronoamperometry, resolves the issue of parasitic current by removing the scanning potential. Instead, the potential applied to one IDA electrode is stepped from ground to the oxidation potential while the potential applied to the other electrode is stepped from ground to the reduction potential. Thus, the limiting current is generated immediately, and the parasitic current due to the initial potential steps disappears quickly [38]. Due to these benefits, chronoamperometry was used in this work.

To achieve the electrochemical detection of redox species using chronoamperometry, a four-electrode electrochemical cell is utilized. The IDA electrodes serve as the working electrodes (anode and cathode), which are referred to as working electrode 1 (WE1) and working electrode 2 (WE2). IDA working electrodes have been fabricated with a variety of materials. The electrodes should be inert, conductive, and stable in solution without oxidizing at the applied potential. Typically, metals such as platinum (Pt) [36, 126], gold (Au) [123, 128], and carbon
have been used for the IDA electrodes. In this work, Au was selected due to its capacity for fabrication by electroless plating and selective removal, as demonstrated in Chapter 4.

In order to apply the correct oxidation and reduction potentials to the working electrodes, a reference electrode (RE) is needed to maintain the potential of the target solution [129]. A variety of materials have been used for the reference electrode including standard hydrogen electrode (SHE) [131], silver/silver chloride (Ag/AgCl) [34, 126] and saturated calomel electrode [132]. The Ag/AgCl electrode has several advantages over other reference electrodes, including the absence of toxic elements like mercury. Additionally, Ag/AgCl electrodes can be easily prepared by microfabrication processes such as electroplating. For example, a silver wire can be formed by electroplating silver ions onto a gold electrode. Subsequently, the silver electrode is immersed in solution containing Cl ions to form a precipitate of AgCl on its surface [131]. As a result of these benefits, Ag/AgCl was selected as the reference electrode for this work. The final electrode in the four-electrode cell is the auxiliary electrode (AE). This electrode allows current to flow through the cell without polarizing the reference electrode, which could lead to a drift in the applied potentials and thus reduced accuracy of the sensor response [129]. The material requirements for the auxiliary electrode are the same as the working electrodes, thus the AE is typically produced from the same material as the working electrodes, which is gold in this case.

To facilitate the electrochemical reaction using the four-electrode cell for detection of redox species using chronoamperometry, an electrochemical control and detection circuit was developed. The major functions of the control and detection circuit are to provide the appropriate oxidation and reduction potentials to the IDA working electrodes, to apply potential to the reference electrode so as to maintain the potential of the solution, to allow the auxiliary electrode
to make electrical contact with the solution to complete the electrochemical cell, and to provide
detection and amplification of the sensor current generated during the redox reaction. The control
and detection circuit for the electrochemical sensor was realized by developing a hybrid circuit
as shown in Figure 5.3. The potential at the cathode (WE2) is determined by the switch
configuration, thus it can be alternated between ground and the reduction potential given by the
voltage supply. The potential at the anode (WE1) is also determined by the switch configuration,
thus it can be alternated between ground and the oxidation potential through the connection to
Op-amp 1. The Ag/AgCl reference electrode (RE) is held at ground by connection to the
inverting terminal of Op-amp 2, which is fixed at ground by grounding the non-inverting
terminal [133]. To avoid current flowing through RE and thus causing drift in its potential, the
AE is connected to the output of Op-amp2.
The operation of the control and detection circuit is as follows. A droplet of solution containing target analyte is placed on the sensor while the switch is set to the “off” position, thus WE1 and WE2 are at ground potential vs. RE. The switch is then flipped to the “on” position, thus the oxidation and reduction potentials are applied to WE1 and WE2, respectively. The species to be detected is oxidized and reduced at the working electrodes, generating current at WE1 and WE2. The current appearing on WE1 is converted to voltage and amplified by Op-amp 1, which is in I-V conversion setup with feedback resistor $R_1$. Thus the sensor current is converted to voltage signal with amplification determined by the choice of resistor value. The
voltage signal is then input into the instrumentation amplifier where it is compared to the baseline voltage as determined by $V_{ox}$. The difference between the two signals is amplified by choice of resistor $R_G$ [134]. The output voltage from the instrumentation amplifier can then be measured, and the overall I-V conversion is given by the equation

$$I = \frac{V_o}{(1 + \frac{50k\Omega}{R_G})R_i} \quad (4).$$

The discrete components used in the control and detection circuit were selected for their optimum performance characteristics. For controlling the potentials applied to the working, reference, and auxiliary electrodes, an OPA129 Ultra-low Bias Current Difet Operational Amplifier (Texas Instruments/Burr Brown) was chosen. The OPA129 was also used for detection of the sensor current through I-V conversion. This device provides ultra-low bias current (100 fA max), low offset (2 mV max), and low drift (10 µV/°C max) by using dielectrically-isolated FET inputs [135]. After I-V conversion, the voltage signal is amplified with a second stage instrumentation amplifier. For the instrumentation amplifier, an INA116 Ultra Low Input Bias Current Instrumentation Amplifier (Texas Instruments/Burr-Brown) was selected due to its low input bias current (3 fA typ), low offset voltage (2 mV max), and high common-mode rejection (84 dB, G=10) [134].

The design layout for the electrochemical sensor is shown in Figure 5.4. A four-electrode setup is used with IDA working electrodes (WE1 and WE2), reference electrode (RE), and auxiliary electrode (AE). The sensor region (Figure 5.4b) contains the IDA working electrodes, which are contained in an area 100 x 100 µm, as well as the RE and AE. The working electrodes are 65 µm long with 30 µm overlap.
Figure 5.4. Schematic diagram of the electrochemical biosensor: (a) diagram of four-electrode layout; (b) higher magnification view of sensor region showing IDA working electrodes, reference electrode, and auxiliary electrode.

To fabricate the nIDA electrochemical biosensor, a two-step micro and nanofabrication process was developed (Figure 5.5). First, electrodes are fabricated in IDA format using the electroless plating with selective removal technique, which was described in Chapter 4. Briefly, polymer templates were produced by nanoinjection molding with cyclic olefin copolymers (COC). The COC templates were activated with a catalyst and then Au was deposited by electroless plating. After mechanically wiping the template surface, electrodes were formed in the template patterns. After fabricating the nIDA electrodes, photolithography was used to create contacts, traces, and pads for interfacing with the nIDA, as well as to create the reference and counter electrodes. The polymer templates containing nIDA electrodes were coated with photoresist (Shipley S1818) at 500 RPM for 10 s and 3000 RPM for 45 s. After softbake in 90°C
oven for 20 minutes, the templates were exposed through a glass-chrome mask with UV light source (MJB3, Karl Suss). The photoresist patterns were developed in 1:4 solution of Microposit 351 and DI water. A thin film of Au (1000 Å) was deposited on the patterned template by e-beam evaporation (Temescal FC1800) and liftoff was achieved by placing the template in acetone solution for 10 minutes. To prepare the reference electrode, an electroplating procedure was used. Ag plating solution (Silver Cyless, Technics) was used with a platinum foil as anode, and the cathode was connected to the electrode to be plated. After plating for 10 seconds at 0.7 mA, the template was removed and polarity reversed before plating in 1 M KCl solution for 7 seconds at 0.7 mA.
To verify that the nIDA sensor results in an increased limiting current and improved detection limit, IDA sensors of varying electrode spacing (800 nm – 3 µm) were fabricated using the described fabrication method. Additionally, a conventional micro-scale IDA (mIDA) sensor was also fabricated using standard photolithography techniques for comparison. For the mIDA sensor, standard photolithography and etch processes are used to create the working electrodes,
reference electrode, and auxiliary electrode. A thin gold film (1000 Å) was deposited by e-beam evaporation (Temescal FC1800) on an unpatterned COC substrate. Next, photoresist (Shipley S1818) was spin-coated at 500 RPM for 10 seconds and 3000 RPM for 30 seconds. After baking in 90 °C oven for 20 minutes, the chip was placed in a mask aligner (Karl Suss MJB3) for exposure through a glass-chrome mask with UV light source. After exposure for 12 seconds, the chip was developed in 1:4 (Microposit 351 developer: de-ionized water) solution for 30 seconds and dried in nitrogen flow. The COC/Au/photoresist complex was then dipped in gold etch solution for 1 minute to remove the exposed gold areas. After rinsing in de-ionized water, the residual photoresist was stripped in acetone, resulting in micropatterned gold on COC. The Ag/AgCl RE was prepared by electroplating one of the patterned microelectrodes. Ag plating solution (Technics) was used with platinum foil as anode, and the cathode was connected to the electrode to be plated. After plating for 10 seconds at 0.7 mA, the chip was removed and polarity reversed before placing in 1 M KCl solution for 7 seconds plating step at 0.7 mA.

5.3 Experimental Results

The results from fabrication of the electrochemical sensors are shown in Figure 5.6. The sensor chip is approximately 2 x 2 cm and contains contact pads for electrical connection to the IDA sensor region (Figure 5.6a). In order to apply the fabricated sensors for detection of target molecules in solution, the IDA working electrodes, reference electrode, and auxiliary electrode must be exposed to the analyte solution while the electrical pads connecting the sensor to the control and detection circuit are protected to prevent short-circuits. To accomplish this, photoresist (Shipley, S1818) was spin-coated, exposed, and developed to open a small window over the sensor region, whereas the rest of the chip remained covered with resist (Figure 5.6b).
Several different combinations of IDA electrode geometries (gap x width) were fabricated for the IDA sensors (Figure 5.6c-f), including 850 nm x 1 µm, 1.5 µm x 600 nm, 3 µm x 600 nm, and 20 µm x 20 µm.
Figure 5.6. Results from fabrication showing: (a) chip-scale photograph of electrochemical sensor (scale bar = 1 cm); (b) optical micrograph of four-electrode layout (scale bar = 500 µm). Optical micrographs of different IDA working electrode combinations (gap x width, scale bars = 10 µm): (c) 850 nm x 1 µm; (d) 1.5 µm x 600 nm; (e) 3 µm x 600 nm; and (f) 20 µm x 20 µm.
The performance of the detection circuit was verified prior to its use with the electrochemical sensor. Component values for the detection circuit \((R_f = 11.5 \, \text{M}\Omega, \, R_G = 4.76 \, \text{k}\Omega)\) were selected to achieve maximum gain while maintaining the stability of the circuit. To simulate the current generated by the sensor during the electrochemical reaction, a current source (Hewlett-Packard 6825A Bipolar Power Supply) was connected to the electrical lead for the working electrode 1, as shown in Figure 5.7a. The voltage response of the circuit to input current was predicted by rearranging equation 4:

\[
V = I \times (1 + \frac{50k\Omega}{R_G}) \times R_f \quad (5)
\]

Currents ranging from below 1 nA to above 100 nA were generated using the current source and the output voltage of the detection circuit was measured with a digital multimeter (Agilent 34401A). The resulting I-V relationship between input current and output voltage is shown in Figure 5.7b along with the values predicted by equation 5. The results show linear response of the detection circuit output voltage to input current over the tested range, which closely matched the expected values.
Figure 5.7. Verification of detection circuit: (a) schematic diagram showing experimental setup; (b) experimental results showing voltage response of detection circuit to input current.
The target molecule used for detection with the electrochemical sensor was polyaminophenol (PAP). Test solutions with PAP concentrations ranging from 1 mM to 1 nM were prepared by the following method. A packet of phosphate buffered saline powder (PBS, Sigma P-3813, pH 7.4) was dissolved in 1 L de-ionized water to generate 0.01 M PBS buffer. Next, 0.109 g of 4-aminophenol (98%, Sigma-Aldrich A71328) was added to 100 mL of the buffer solution to create 10 mM PAP solution. Successive dilution of the 10 mM PAP solution in buffer was performed to produce concentrations ranging from 1 mM to 1 nM (10^{-3}-10^{-9} M) PAP.

For each experiment, a 10-20 μL droplet of PAP solution was pipetted onto the IDA sensor while the switch was in the “off” position. The switch was then turned “on”, thus the oxidation and reduction potentials were applied to WE1 and WE2, respectively. The oxidation and reduction potentials for PAP were set to +350 mV and -350 mV vs. Ag/AgCl reference electrode, respectively [94]. The output voltage from the detection circuit was recorded with a digital oscilloscope (Tektronix TDS 3052 Digital Oscilloscope). This process was repeated for each IDA sensor for the entire range of the PAP concentrations.

The results from electrochemical detection of PAP using nIDA (850 nm gap x 1 μm width) and mIDA (20 μm gap x 20 μm width) sensors are shown in Figure 5.8. For both sensor types at 10^{-3} M, the output voltage stabilized within 10 seconds of the reaction start time, and the signal remained stable (less than 2% variation) for the remainder of the experiment (over 90 s). As expected, the output voltage from the detection circuit showed a reduction by a factor of 10 for each order of magnitude decrease in PAP concentration. Additionally, the voltage response of the nIDA sensor at each concentration was significantly higher than the voltage response of the mIDA sensor.
Figure 5.8. Output waveform from digital oscilloscope showing voltage response as a function of time for: (a) nIDA biosensor and (b) mIDA biosensor at different PAP concentrations.
The output voltage from each experiment was used to calculate the sensor current generated by the sensors using equation 4. The resulting sensor current as a function of PAP concentration was determined for all four sensors and plotted in Figure 5.9. As expected, each sensor displayed linear dependence of current with respect to analyte concentration. For the IDA sensors fabricated by the newly developed technique, the minimum detected concentration was 1 µM, whereas the minimum detected concentration for the traditional mIDA sensor was 10 µM. These values do not represent the ultimate detection limit of each sensor, which would have occurred at intermediate concentrations between the prepared PAP dilutions. To estimate the detection limits, the current response of each sensor to buffer solution without PAP was experimentally measured and used as the baseline for estimating the detection limits of each sensor. The current response of each sensor was then extrapolated to project the estimated detection limit, as shown in Figure 5.9. The estimated detection limit for each sensor is shown in Table 5.1.
Figure 5.9. Current response of electrochemical sensors as a function of target PAP concentration for IDA sensors with varying electrode gap.

Table 5.1. Comparison of different IDA configurations regarding sensor current and estimated detection limit.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Gap</th>
<th>W</th>
<th>M</th>
<th>I vs. mIDA</th>
<th>Det. Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>850 nm</td>
<td>1 µm</td>
<td>25</td>
<td>6.3</td>
<td>3 x 10⁻⁷ M</td>
</tr>
<tr>
<td>B</td>
<td>1.5 µm</td>
<td>600 nm</td>
<td>24</td>
<td>3.9</td>
<td>6 x 10⁻⁷ M</td>
</tr>
<tr>
<td>C</td>
<td>3 µm</td>
<td>600 nm</td>
<td>12</td>
<td>2.5</td>
<td>8 x 10⁻⁷ M</td>
</tr>
<tr>
<td>D</td>
<td>20 µm</td>
<td>20 µm</td>
<td>2</td>
<td>1</td>
<td>2 x 10⁻⁶ M</td>
</tr>
</tbody>
</table>
As expected, decreasing the gap between electrodes had a significant impact on the detection limit of the IDA sensors. The best sensing performance was achieved with sensor type “A”, which demonstrated a 6.3x increase in sensor current over the mIDA sensor produced by photolithography (sensor type “D”). This resulted in an estimated detection limit of $3 \times 10^{-7}$ M, thus the nIDA sensor achieved almost an order of magnitude improvement in detection limit over the mIDA sensor (estimated detection limit of $2 \times 10^{-6}$ M). According to the equation describing the current generated at IDA electrodes (equation 1), the nIDA sensor should generate more current than the mIDA sensor at a given concentration of analyte. By inserting the electrode array geometries for the mIDA sensor ($w = 20 \, \mu m$, $g = 20 \, \mu m$, $m = 2$) and the “nano A” sensor ($w = 1 \, \mu m$, $g = 850 \, nm$, $m = 25$) into equation 1, the ratio between the generated currents can be predicted. This analysis indicates the nIDA sensor should generate approximately 13 times more current than the mIDA sensor at a given concentration. The difference between the theoretical prediction of 13x increase in current and the experimentally measured 6.3x increase in current of the nIDA over the mIDA is likely the result of several factors. Equation 1 was developed with several assumptions, including (a) that the IDA finger width is much smaller than the finger length and (b) that the IDA is composed of many electrodes so edge effects have negligible influence on the sensor current [37]. These assumptions do not hold true for the mIDA sensor. Additionally, it is possible that some of the electrodes in the nIDA contained open circuits due to inhomogeneity in the fabrication process, thus reducing the number of active fingers in the array. Furthermore, misalignment during the photolithography step, which is used to create contacts, traces, and pads for interfacing with the nIDA, could result in electrodes being excluded from the array, which would reduce the current generated at the nIDA sensor.
As described earlier, one of the major benefits of the nIDA sensors described in this work is their potential for mass-production at low-cost, which is not feasible with other fabrication techniques, such as electron beam lithography (EBL). To demonstrate the improvements in processing time and costs, an estimate was made for the cost and lithography time required to produce nIDA biosensors by the newly developed method as well as by the traditional EBL method. The costs were estimated using industry pricing guides and the rates for equipment usage in the Engineering Research Center Clean Room at the University of Cincinnati. The processing time was estimated on the basis of lithography time for producing a nIDA pattern by EBL (including focusing, write-field alignment, and pattern write-time) or nanoinjection molding with pre-fabricated mold. Table 5.2 shows the resulting estimate of the critical costs and processing times required for fabricating a sensor with the newly developed technique along with the same parameters given for a device fabricated by EBL for comparison. The total cost of the nanobiosensor fabricated by the proposed method is almost an order of magnitude lower than the total cost of the same nanobiosensor fabricated by the traditional method. Additionally, the processing time is also an order of magnitude lower than the traditional method.

Table 5.2. Comparison of critical parameters such as processing time and costs associated with nIDA sensors fabricated by e-beam lithography and the newly developed method.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>EBL</th>
<th>This Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithography Time</td>
<td>30 min</td>
<td>1 min</td>
</tr>
<tr>
<td>Cost</td>
<td>$23</td>
<td>$3</td>
</tr>
</tbody>
</table>
It is anticipated that the mass-producible nIDA sensor will be used in disposable applications in conjunction with a portable miniaturized analysis system. The hybrid circuit developed in this work is suitable for such a system due to its simple user interface, including an on/off switch and output voltage signal, which can be easily miniaturized in a portable format. Such a portable system would cost approximately $50 using standard, commercially available parts, including breadboard, integrated circuits, and voltage readout display.

5.4 Conclusions

In this section, a new approach was described for the realization of mass-producible electrochemical nanobiosensors. The new method utilizes a two-step micro- and nano fabrication approach to create a four-electrode electrochemical sensor with nIDA working electrodes. A control and detection circuit was developed for use with the biosensor in an amperometric sensing scheme for the detection of redox species. The nanoelectrode-based biosensor was applied for detection of redox couple PAP-PQI, and its performance compared with a traditional mIDA sensor. The nIDA sensor showed improvement in the current response and detection limit when compared with mIDA sensor. Additionally, the use of the high-throughput electrode fabrication method described in Chapter 4 enables the development of mass-producible sensor chips that significantly reduce the cost and processing time associated with nanobiosensors.
CHAPTER 6

CONCLUSIONS
6.1 Summary

This thesis has described the research and development of mass-producible nanotechnologies, including nanoparticle assemblies, nanoelectrodes, and nanobiosensors. To achieve these goals, a new nanofabrication platform was established that couples the precision and throughput of polymer injection molding with the simplicity of template-driven assembly. High-throughput nanoinjection molding technology was developed, characterized, and applied for the fabrication of polymer substrates with nanostructured surfaces. The nanostructured polymers were then used as templates for the assembly of nanoparticles and patterning of nanoelectrodes. Finally, the templates were used for the realization of a mass-producible electrochemical nanobiosensor that is combined with custom detection circuitry for the ultra-sensitive detection of biomolecules.

For the development of nanoinjection molding technology, the fabrication of nano-scale mold structures on a replaceable Ni mold disk was described and results were given for production of 1D and 2D mold structures. The mold patterns were used for successful replication of polymer templates using injection molding with cyclic olefin copolymers (COC). The fidelity of pattern transfer from the mold structures to the polymer templates was studied, showing excellent reproducibility in the range of 300 nm – 1 µm. Additionally, mold features in the range of 300 nm – 1 µm were shown to be durable for 200 injection cycles, indicating the suitability of this approach for mass-production of nano-scale features in polymer templates.

The polymer templates were applied for the realization of nanoparticle assemblies on solid substrates. A new nanoparticle assembly technique was developed involving deposition of nanoparticles on a polymer template and their selective removal by a mechanical wiping process. Results were demonstrated for the assembly of multiple sizes and types of nanoparticles in both
1D and 2D template patterns. The dimensions of the template patterns were used to control the number, size, and type of nanoparticles in an assembly. Since the template fabrication method and subsequent assembly technique are both rapid, high-throughput processes, this approach may enable the mass-production of nanoparticle-based devices for commercial applications.

The polymer templates produced by nanoinjection molding were also used to produce nanoelectrodes. Deposition and selective removal of metal films using electroless plating was used to achieve Ag and Au patterns on the polymer templates. Electrodes with feature sizes ranging from 300 nm – 1 µm were demonstrated in array format over lengths scales approaching 1 mm. The electrodes were shown to be conductive and electrically isolated with linear I-V characteristics.

Finally, the polymer templates were used as part of an integrated micro- and nanofabrication process for the realization of mass-producible electrochemical nanobiosensors. The new method utilizes a two-step micro- and nano fabrication approach to create a four-electrode electrochemical sensor with nano interdigitated array (nIDA) working electrodes. A hybrid control and detection circuit was developed for use with the biosensor in an amperometric sensing scheme for the detection of redox species. The nIDA biosensor was applied for detection of redox couple PAP-PQI, and its performance compared with a traditional micro interdigitated array (mIDA) sensor. The nIDA sensor showed improvement in the current response and detection limit when compared with mIDA sensor. Additionally, the use of high-throughput electrode fabrication methods enabled a significant reduction in the cost and processing time associated with nanobiosensors when compared to other electrode fabrication techniques, such as electron beam lithography.
6.2 Suggestion for Future Work

This thesis has focused on the development of mass-producible fabrication techniques that were applied for the realization of specific nano-scale structures and devices. As such, there are several aspects of this work that can be further investigated.

The nanoinjection molding process developed in this work was used for production of polymer templates in cyclic olefin copolymers (COC). The mold used for producing polymer templates by nanoinjection molding is a critical factor in determining minimum features that can be produced. Optimized mold processing should enable the production of sub-100 nm features in polymer templates for subsequent patterning and device applications. Additionally, there are a wide range of thermoplastic polymers that can be injection molded, including polymethylmethacrylate (PMMA) and polycarbonate (PC), thus the nanoinjection molding process can be applied to produce polymer templates of materials other than COC. Furthermore, nanostructured polymer substrates developed by nanoinjection molding may have an impact on a wide range of other fields, including use as nanochannels for nanofluidic systems, gratings for photonic devices, and scaffolds for tissue engineering.

The template-assisted assembly method developed in this work was used for the assembly of silica and antimony (V) oxide nanoparticles on the polymer templates. Due to the significant interest in nanoparticles and nanoparticle assemblies, there exists a wide range of nanoparticle types and sizes, including organic, inorganic, metallic, and semiconducting nanoparticles. Thus, the assembly of other types and sizes of nanoparticles can be studied and optimized for specific applications, including optical and electronic devices as well as multifunctional surfaces. Additionally, there is significant interest in the assembly of other nanoscale materials, such as carbon nanotubes (CNTs), on solid substrates for a range of electronic
and biosensing device applications. Thus, the techniques developed in this work may be applied as a general platform for the study of nano-scale assembly.

The deposition and selective removal technique was also applied for the patterning of silver and gold films deposited by electroless plating, resulting in the formation of nanoelectrodes in the polymer template. A variety of metals can be deposited by electroless plating methods, including copper (Cu), nickel (Ni), iron (Fe), palladium (Pd), rhodium (Rh), ruthenium (Ru), platinum (Pt), tin (Sn), and lead (Pb). Therefore, the patterning of a wide range of electrode materials can be studied using the newly developed techniques.

The mass-producible electrochemical sensor described in Chapter 5 has been demonstrated for improved detection of reversible redox species poly-aminophenol (PAP). Since PAP is widely used as a target molecule for immunoassays, the newly developed sensor could be combined with additional assay components (such as antibodies and enzyme layer) for detection of non-electrochemically active species. Additionally, the sensor could be combined with polymer microchannels for a fully integrated lab-on-a-chip system.
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