Generating arrays of nanoring structures : chemical lithography with 2-dimensional polymeric colloidal crystals

Zhao, Qin

2014

Zhao, Q. (2014). Generating arrays of nanoring structures : chemical lithography with 2-dimensional polymeric colloidal crystals. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/59530>

<https://doi.org/10.32657/10356/59530>

**GENERATING ARRAYS OF NANORING STRUCTURES:
CHEMICAL LITHOGRAPHY WITH 2-DIMENSIONAL
POLYMERIC COLLOIDAL CRYSTALS**

**ZHAO QIN
SCHOOL OF MATERIALS SCIENCE AND ENGINEERING
2014**

**GENERATING ARRAYS OF NANORING STRUCTURES:
CHEMICAL LITHOGRAPHY WITH 2-DIMENSIONAL
POLYMERIC COLLOIDAL CRYSTALS**

ZHAO QIN

School of Materials Science & Engineering

A thesis submitted to Nanyang Technological University
in fulfilment of the requirement for the degree of
Doctor of Philosophy

2014

Acknowledgements

First of all, with sincere regards I would like to thank my supervisor Assoc. Prof. Wong Chee Cheong for the invaluable support, guidance and inspiration throughout the research. The present work at every stage bears the impression of his wise counsel, concrete suggestions and criticisms. His encouragement and constant advice helped me in the smooth progress of this project. I have been under Prof Wong's mentoring from the very beginning of my research experience when I was a third year undergraduate research student. Not only in the research activities, has he influenced me in all the aspects of my life during these years, especially his savoir-vivre and the confidence in problem solving. For me, he is not only a supervisor in research work; he is also a respected family elder and good friend in my life.

Meanwhile, I am especially thankful to all my colleagues working in Prof Wong's group, Anantha, Ankit, Eric, Husen, Lee Kwang Hong, Leng Bing, Ong Duen Yang, Wang Xiu, Yip Chan Hoe and Zhang Jing Jing. Despite their busy schedules they have always been supportive and have provided me with a lot of suggestions. The discussions I have had with the group have helped me gain various perspectives to my work. Their kindness and inspiration has definitely helped me do a lot better at my work.

Last but not least, I would like to thank all my friends who have supported me throughout my research career. I am also grateful to my parents with fervent gratitude for being a source of continued support and motivation which has always helped me gain an optimistic view in me and an enthusiastic approach throughout my educational career. Sincerely thank to my husband, Mr. Fei Liyuan, he always give me confidence when I am in down time.

Table of Contents

Acknowledgements	i
Table of Contents	ii
List of Figures	iv
List of Tables.....	viii
List of Common Abbreviations.....	ix
Summary	x
CHAPTER 1: Introduction.....	1
1.1 Background	1
1.2 Optical Behaviors of Nanoring Arrays: A Brief Review	3
1.3 Motivations	9
1.4 Objective and Scopes	11
1.5 Organization of thesis.....	12
CHAPTER 2: Fabrication of Nanoring Arrays – A Review.....	14
2.1 Nanofabrication Techniques.....	14
2.1.1 Optical Lithography.....	14
2.1.2 Direct Writing Technique	15
2.1.3 Soft Lithography.....	16
2.1.4 Nanosphere Lithography	16
2.2 Fabrication of Nanosphere Colloidal Crystals	17
2.2.1 Drop Coating Method.....	18
2.2.2 Dip Coating Deposition.....	19
2.2.3 Spin Coating Technique.....	20
2.2.4 Assembly at Interfaces.....	21
2.3 Fabrication of Nanoring Arrays by Nanosphere Lithography	21
2.3.1 Ion Polishing and Electron Deposition.....	22
2.3.2 Capillary and Edge Spreading Infiltration.....	25
2.3.3 Localized Dewetting.....	26
CHAPTER 3: Ring Shaped Footprint Arrays from 2D Polymeric Colloidal Crystals	29
3.1 Fabrication of Polymeric Nanosphere Monolayers by Rapid Ethanol Spreading.....	29
3.1.1 Synthesis of Polymeric Colloidal Nanospheres.....	30
3.1.2 Preparing Monolayers of Polymeric Nanospheres	32
3.2 Formation of Ring Shaped Footprints through Localized Accumulation of Nanosphere Surface Molecules	36
3.3 Chapter Summary.....	39
CHAPTER 4: Forming Nanoring Arrays with Assistance of Bridging Molecules	41

4.1 Fabricating Nanoring Arrays with Assistance of APTES Treatment.....	42
4.2 Prerequisites for Bridging Molecules.....	49
4.3 Influences of APTES Treatment Conditions	52
4.3.1 Coating Dynamics of APTES on Silica Surfaces	52
4.3.2 Influences on Nanoring Morphologies by Treatment Conditions of APTES Molecules	59
4.4 Chapter Summary.....	62
CHAPTER 5: Nanoring Fabrication in Alternative Systems	64
5.1 Nanoring Formation by Alternative Template Nanospheres	64
5.2 Effects of Template Nanospheres on Nanoring Formation	68
5.2.1 Geometrical Dependence on Template Nanosphere Size	68
5.2.2 Stabilizing Surfactant Molecules Introduced During Nanosphere Synthesis	73
5.2.3 Charged End Groups of Polymer Chains Introduced During Nanosphere Synthesis.....	76
5.3 Fabrication of Nanoring Arrays on Alternative Substrates.....	78
5.4 Metallic Nanoring Structures	82
5.5 Chapter Summary.....	83
CHAPTER 6: Manipulating Nanoring Morphologies by Tailored Swelling of Template Nanospheres	85
6.1 Effects of Relaxation Time on Nanoring Formation	85
6.2 Enhanced Swelling of Template Nanospheres by Solvent Vapor Annealing	90
6.2.1 Solubility Parameter Mediated Mixing Behaviors	90
6.2.2 Experiment Set-up for Vapor Annealing.....	92
6.2.3 Effects of Acetone Vapor Annealing.....	92
6.2.3 Effects of Toluene Vapor Annealing.....	96
6.2.4 Potential for Generation of Multi-ring Structure by Vapor Annealing	99
6.3 Accelerated Relaxation of Template Nanospheres by Thermal Annealing	101
6.4 Chapter Summary.....	104
CHAPTER 7: Conclusions and Future Work.....	106
7.1 Conclusions	106
7.2 Recommendations for Future Work	109
7.2.1 Improving Efficiency of Surface Molecular Transfer	109
7.2.2 Controlling Orientation of Nanoring Array	109
7.2.3 Diversifying Morphology of Nanoring Array	110
7.2.4 Exploring Production and Application of Functional Nanoring Arrays	111
REFERENCES	113
APPENDIX: Publications and Conferences	124

List of Figures

Fig 1- 1. Schematic illustrations of (A) a unit cell representing a hexagonal array of nanorings, (B) geometrical specifications of a specific nanoring.	3
Fig 1- 2. (A) FDTD simulated transmission spectrum of a typical hexagonal gold nanoring array with specifications listed in Table 1-1. (B) & (C) FDTD simulated charge density distributions for this gold nanoring array at (B) antibonding wavelength, (C) bonding wavelength. (Unpublished work by author)	5
Fig 1- 3. FDTD simulated transmission spectra for hexagonal gold nanoring arrays with different ratios between the ring thickness and the outer diameter (t/d_o). (Unpublished work by author)	6
Fig 1- 4. FDTD simulated transmission spectra for hexagonal gold nanoring arrays with different lattice constants. (Unpublished work by author).....	8
Fig 2- 1. (A) Schematic view of colloidal nanosphere assembly in a sessile drop on a horizontal substrate. (B) A captured image from a real time study of nanosphere assembly in drop coating process (unpublished work by author).	18
Fig 2- 2. (A) Schematic view of colloidal nanosphere assembly by vertical deposition. (B) Photograph of the set-up for dip coating deposition, which involves the assistance of a pump to remove the suspension (original work from the author). (C) Photographic image and (D) Cross sectional FESEM image of colloidal crystals obtained by dip coating method (unpublished work by author).	19
Fig 2- 3. Schematic view of colloidal nanosphere assembly by spin coating technique.....	20
Fig 2- 4. Assembly of nanospheres into 2D colloidal crystal at interface.....	21
Fig 2- 5. (A) Fabrication of nanoring array by etching the target material with the non close packed nanospheres as the etching mask. (B) Fabrication of nanoring structures by etching the non close packed template nanospheres which are passivated by a passivative layer deposited in the interstitial regions. (C) Nanoring array formed by electron deposition of target material inside the ring shaped groove structures created by manipulating the template 2D nanosphere monolayer.	24
Fig 2- 6. (A) Fabrication of nanoring arrays by localized capillary infiltration of target solutes through evaporation or heat treatment of the patterning suspension. (B) Generation of nanoring structures by infiltration of target molecules through guided reactive edge spreading of the molecules along the template nanosphere surfaces.....	26
Fig 2- 7. Formation of nanoring arrays by localized dewetting of polymer films based on a micro contact printing approach.....	27
Fig 3- 1. (A) Procedure to fabricate monolayers of polymer nanospheres by rapid ethanol spreading. (B) A monolayer of 260nm PS nanospheres floating on the water surface before transferring to substrates. Top view (C) and side view (D) FESEM images of the monolayer transferred onto a silica substrate.	33
Fig 3- 2. Photographic images of nanospheres spreading on water/air interface by dispersing the PS nanospheres in water/ethanol mixtures at ethanol fraction of (A) 100%, (B) 80%, (C) 50%, and (D) 20%.	35
Fig 3- 3. Deformation in the shape of the water/air interface caused by the buoyancy and particle weight.....	36

Fig 3- 4. (A) 3D view and (B) 2D view of the ring shaped footprint left over on silica substrate after peeling off a 260nm PS nanosphere monolayer, (C) The cross section profile of a remnant ring(red, measured) matches with a 260nm circular nanosphere outline(white, drawn). The scale bar is 100nm. ..	39
Fig 4- 1. Basic procedure to generate an array of nanorings. (A) Nanosphere monolayer stored in atmosphere after fabrication, and the surface molecules relax during storage. (B) APTES treatment applied to the monolayer to improve the final ring features. (C) Nanoring array obtained after peeling off the monolayer template.	43
Fig 4- 2. (A) Chemical structure of an APTES molecule. (B) A typical hydrolysis reaction of one APTES molecule with three water molecules.....	43
Fig 4- 3. (A) Covalent bonding and (B) hydrogen bonding between the functional groups of APTES molecules and the hydroxyl groups on substrate surface. (C) Horizontal polymerization among surface bonded APTES molecules. (D) Vertical polymerization among the molecules in solution with the surface bonded molecules. (E) Cyclic reactions occurred for APTES molecules coated on substrate surface.....	45
Fig 4- 4. (A) 3D and (B) 2D view of the nanorings obtained by a 260nm PS nanosphere monolayer on silica substrate after 1 hr treatment in ethanol solution of 1vol% APTES.....	46
Fig 4- 5. Cross section profiles of nanorings on silica substrates templated by 260nm PS nanosphere monolayers (A) without (B) with APTES treatment before peeling off the nanospheres.....	47
Fig 4- 6. FTIR absorption spectrum of a nanoring sample prepared with APTES treatment.	48
Fig 4- 7. (A) 3D and (B) 2D AFM images of a nanoring array on silica substrate generated by a monolayer of 260nm PS nanospheres after 1 hr treatment in absolute ethanol.	49
Fig 4- 8. (A) Molecular structures of MPTMS, Cysteamine and OTMS. (B) 2D and (C) 3D view of the nanorings on silica substrate obtained by a monolayer of 260nm PS nanospheres after treatment in ethanol solution of 1vol% MPTMS for 1 hr.....	51
Fig 4- 9. Measured contact angles of water droplets on silica substrates after APTES treatments with various concentrations for time durations until 300min.	54
Fig 4- 10. Contact angles of water droplets on silica substrates after treatments with various APTES concentrations for time duration within 60min.	55
Fig 4- 11. FESEM images of gold nanoparticles adsorbing on silica substrates with treatment of 1% APTES for time duration of (A) 2 min, (B) 5 min, (C) 10 min, (D) 20 min, and (E) 60 min. The scale bars are 100 nm.	56
Fig 4- 12. 3D AFM images of nanorings on silica substrate generated by 260nm PS nanosphere monolayers after treatment with 1vol% APTES in ethanol solution for (A) 10 min, (B) 1hr, and (C) 3hr. (D) Comparison among the cross section profiles of nanorings generated with APTES treatment of various time durations.....	60
Fig 4- 13. 3D AFM images of nanorings on silica substrate generated by 260nm PS nanosphere monolayer after 10min treatment with ethanol solution of APTES in concentration of (A) 1% and (B) 10%.	61
Fig 4- 14. 3D AFM images of nanoring arrays on silica substrate generated by 260nm PS nanosphere monolayers after 1hr treatment with ethanol solution of APTES in concentration of (A) 1%, (B) 10%, and (C) 15%. (D) Comparison among the cross section profiles of nanorings generated with APTES treatment of various concentrations.	62

Fig 5- 1. (A) 2D AFM image, (B) 3D AFM image and (C) cross section profile of nanorings on silica substrate templated by a monolayer of 280nm PMMA nanospheres, the monolayer was treated with 1% APTES in ethanol solution at room temperature for 1 hr. The scale bar in the inset is 100nm.	66
Fig 5- 2. (A) FESEM image of a template silica nanosphere monolayer. (B) AFM images of the remnants on silica substrate templated by a monolayer of 320nm silica nanospheres after treatment in ethanol solution of 1vol% APTES for 1 hr.....	67
Fig 5- 3. Nanoring arrays on silica substrate templated by PS nanospheres in diameter of (A) 165nm, (B) 260nm and (C) 600nm. The scale bars in the insets are 100nm. (D) Schematic illustrations for the side view of the remnant morphology before a template nanosphere was peeled off and the top view of the remnant after the template nanosphere was peeled off. (E) The measured nanoring diameters are plotted as a function of the square root of the diameters of the template nanospheres.	69
Fig 5- 4. 3D AFM images of nanoring arrays on silica substrate generated after 1hr treatment with ethanol solution of 1% APTES by monolayers of PS nanosphere in diameters of (A) 165nm, (B) 260nm and (C) 600nm.	72
Fig 5- 5. (A) 2D and (B) 3D AFM images of the ring shaped footprints left over on silica substrate after directly peeling off a template monolayer of 370nm PS nanospheres without surfactant molecules.	74
Fig 5- 6. (A) 2D AFM image, (B) 3D AFM image and (C) cross section profile of nanorings on silica substrate templated by a monolayer of 370nm PS nanospheres without surfactant molecules, the monolayer was treated with 1% APTES in ethanol solution at room temperature for 1 hr. The scale bar in the inset is 100nm. (D) The measured values of nanoring diameters with regard to 370nm template PS nanospheres without surfactant molecules were fitted into the graph of Fig 5-3(E).	75
Fig 5- 7. (A) 2D AFM image, (B) 3D AFM image and (C) cross section profile of nanorings on silica substrate templated by a monolayer of 340nm positively charged PS nanospheres, the monolayer was treated with 1% APTES in ethanol solution at room temperature for 1 hr. The scale bar in the inset is 100nm. (D) The measured values of nanoring diameters with regard to 340nm positively charged template PS nanospheres were fitted into the graph of Fig 5-3(E).	77
Fig 5- 8. 3D AFM images and cross section profiles for nanoring structures generated on polycarbonate substrates (A, B) without and (C, D) with bridging molecule treatment before removing the templated monolayers of 260nm PS monolayers. All these monolayers were stored in air for 2 weeks before usage, and the bridging molecule treatment was carried out with ethanol solution of 1% APTES for 1hr at room temperature. The scale bars in the insets are 100nm.	79
Fig 5- 9. (A) 2D, (B) 3D AFM images and (C) cross section profile for nanoring structures generated on gold substrates templated by a monolayer of 260nm PS. The monolayer was stored in air for 2 weeks before applied with a treatment in ethanol solution of 1% APTES for 1hr at room temperature. The scale bar in the insets is 100nm.....	81
Fig 5- 10. FESEM images of (A) gold nanorings, (B) inverse gold nanorings fabricated by applying the obtained polymer nanoring arrays as templates. The scale bars in the insets are 100nm.	83
Fig 6- 1. AFM images of remnants on silica substrates obtained by direct peeling off PS monolayers which have been stored in atmosphere ambient for (A) & (B) overnight, (C) & (D) 1 week, and (E) & (F) 2 weeks.....	87
Fig 6- 2. AFM images of remnants on silica substrates templated by PS monolayers which have been stored in atmosphere ambient for (A) & (B) overnight, and (C) & (D) 1 week before being treated with ethanol solution of 1% APTES at room temperature for 1hr.	89

Fig 6- 3. Schematic illustration of the set-up for vapor annealing.	92
Fig 6- 4. 3D AFM images and cross section profiles for nanoring structures generated by 260nm PS monolayers which have been annealed with acetone vapor for (A, B) 30min, (C, D) 60min, and (E, F) 90min. All these monolayers were annealed immediately after drying in air, and all of the annealed samples were treated with 1% APTES for 1hr at room temperature. The scale bars in the insets are 100nm.	93
Fig 6- 5. (A) Cross section profile of the remnant structures generated by a monolayer without annealing, which corresponds to the one shown in Fig 6-2(A&B). (B, C) Cross sectional FESEM images of monolayers annealed with acetone vapor for (B) 60min, and (C) 90min. (D) Schematic illustration about the reduction in effective surface area due to flattened contact area.	94
Fig 6- 6. AFM images and cross section profiles for nanoring structures templated by monolayers of 260nm PS nanospheres which have been annealed with toluene vapor for (A, B) 10min, and (C, D) 30min. All these monolayers were annealed immediately after drying in air, and all of the annealed samples were treated with 1% APTES for 1hr at room temperature. The scale bars in the insets are 100nm.	97
Fig 6- 7. FESEM images of tilted views of monolayers annealed with toluene vapor for (A) 50min and (B) 60min.	98
Fig 6- 8. (A) 2D and (B) 3D AFM images and (C) cross section profile for remnant structures templated by a monolayer of 260nm PS nanospheres which has been annealed with acetone vapor for 90min. The monolayer was stored in air for 2 weeks before annealing, and the annealed sample was treated with 1% APTES for 1hr at room temperature. The scale bar in the inset is 100nm.	100
Fig 6- 9. 3D AFM images and cross section profiles for nanoring structures generated by 260nm PS monolayers which have been annealed at 60°C on a hotplate for (A, B) 1hr, (C, D) 4hr, and (E, F) 8hr. All these monolayers were annealed immediately after drying in air, and all of the annealed samples were treated with 1% APTES for 1hr at room temperature. The scale bars in the insets are 100nm.	103
Fig 7- 1. Prototype to apply the fabricated functional nanoring array as a sensing device.	112

List of Tables

Table 1- 1: Specifications of the lattice constant and the geometrical parameters for a typical hexagonal gold nanoring array discussed by Fig 1-2.....	5
Table 1- 2: List of lattice constants and geometrical parameters of the hexagonal gold nanoring arrays for discussions related to Fig 1-3.	7
Table 1- 3: Specifications of lattice constants and geometrical parameters of the hexagonal gold nanoring arrays for discussions related to Fig 1-4.	8
Table 6- 1. List of solubility parameters.	91

List of Common Abbreviations

AFM	Atomic Force Microscopy
APTES	(3-Aminopropyl) triethoxysilane
FDTD	Finite Difference Time Domain
FESEM	Field Emission Scanning Electron Microscopy
LSPR	Localized Surface Plasmon Resonance
MPTMS	(3-Mercaptopropyl) trimethoxysilane
NIR	Near-infrared
OTMS	Octadecyl trimethoxysilane
PC	Polycarbonate
PMMA	Poly(methyl methacrylate)
PS	Polystyrene
RIE	Reactive Ion Etching
SDS	Sodium Dodecyl Sulfate

Summary

Nanoring arrays have attracted extensive research interest due to the novel and promising applications in a wide range of scientific fields. The limitations of existing fabrication techniques encourage the search for a new method to fabricate nanoring arrays which preserves easy process control and flexible tunability of nanoring geometries. This thesis demonstrates a simple and versatile approach for the fabrication of nanoring arrays by applying polymeric nanosphere monolayers as the templates.

Arrays of well-defined polymeric nanoring features can be obtained by simply treating the template monolayers with molecules which can form disordered molecular networks on the substrate. Formation of nanoring structures is mainly realized by the interpenetration and attractive interactions between such molecular networks and the loosely entangled surface chains due to relaxation of the template nanospheres. Since the treatment molecules act as bridges to anchor surface polymer chains on substrate surface, these molecules are named as ‘bridging molecules’ in this thesis work. The feasibility to transfer the polymeric nanoring patterns into arrays of gold nanoring structures has also been demonstrated, indicating the potential applications of this fabrication technique to produce functional nanoring arrays composed of other materials.

The versatility of this technique has been proven by forming nanoring arrays with alternative bridging molecules, template nanospheres and supporting substrates. Based on a systematic study about the formation mechanisms, some prerequisites for successful formation of nanoring structures have been established. Besides, the nanoring morphologies were shown to be affected by the treatment condition of bridging molecules, molecular structures of

template nanospheres, and surface properties of substrates. A linear relationship between the nanoring diameter and the square root value of the template nanosphere size is derived based on geometrical calculations and experiment verification. Therefore, change in the sizes of the template nanospheres will result in simultaneous change in the diameters of nanoring structures and the lattice constants of nanoring arrays. In addition, vapor annealing or thermal annealing has been carried out to accelerate the relaxation of the template nanospheres and facilitate fast formation of nanoring arrays. Manipulation of the nanoring geometries can be achieved due to the form factor change of the template nanospheres upon annealing. By tailoring the relaxation of template nanospheres based on acetone vapor annealing, formation of multi-ring structures has been demonstrated.

CHAPTER 1: Introduction

1.1 Background

Optical properties of nanostructures have gained extensive research interests in various scientific fields because of the vast promising applications [1-5]. The optical behaviors of nanostructures are dominated by the localized coherent oscillation of the nanostructures' conduction band electrons, named as localized surface plasmon resonance (LSPR). The LSPRs of nanostructures will be sensitively determined by their compositions, geometries and environmental mediums. Up to date, studies based on LSPRs have covered a variety of nanostructures with shapes such as spheres [6], triangles [7], disks [8], crescents [9] and stars [10]. However, the resonant wavelengths for most of these reported nanostructures are shorter than 1000nm. For some complex nanostructures, such as shells [11], rods [12] and rings [13], the optical behaviors are dependent on the coupled plasmonic resonances, which provide a wide range of tuned resonances extending to the near-infrared (NIR) part of the spectrum. Due to this tunability, a large number of important applications have been explored, including optical manipulation of nanoparticles [14], metamaterials [15, 16], optical waveguiding [17, 18], biological or chemical sensing [19], and biomedical applications [20].

Among the nanostructures showing resonances from visible to NIR wavelengths, ring shaped structures are accepted as more reliable nanostructures which are capable to generate stronger LSPRs [21, 22]. At resonant conditions of nanoring structures, significant field enhancements can be achieved. Compared with those observed for the nanorods and nanoshells, the enhanced fields for nanorings are found to be more uniformly distributed inside the cavities

[23]. Besides, another key advantage of nanoring structures is due to the large exposed empty volumes of the cavity which allows incorporation of significant amount of analytes [24]. Therefore, nanoring structures are regarded as effective candidates for the applications of surface enhanced spectroscopies, such as LSPR sensing, Surface Enhanced Raman Scattering (SERS) and Surface Enhanced Infrared Absorption (SEIRA).

Compared with isolated or random distributed nanostructures, periodic arrays of nanostructures are able to provide additional tunability of the physical or chemical properties and show potentials for novel applications, depending on the geometries of the nanostructures and lattice constants of the arrays. For the resonances of periodic nanostructure arrays, it will not only be determined by the plasmon resonances of isolated nanostructures but also be affected by arranging patterns due to near field or far field coupling between adjacent nanostructures [25-28]. Therefore, nanofabrication techniques to generate arrays of nanostructures with well defined geometry, spacing and arrangement have attracted extensive research focuses.

The development of nanofabrication techniques is always driven by the demand of enhanced performance, improved productivity and reduced cost. According to such demand, colloidal lithography has been adopted by increasing number of nanofabrication processes to create large scale of periodic nanostructure arrays [29-32]. It precisely locates the nanostructures into regular patterns by using self assembled colloidal crystals as the templates. Some other commonly used nanofabrication methods consist of optical lithography [33] which crafts bulk materials into nanopatterns, electron-beam (E-beam) lithography [34] or Focused Ion Beam (FIB) technique [35] which directly writes the patterns, and the soft lithography [36] technique which prints the desirable patterns from a pre-generated stamp. Among the variety,

colloidal lithography is accepted as a high throughput and cost effective approach which offers potentials to generate various types of nanostructures.

1.2 Optical Behaviors of Nanoring Arrays: A Brief Review

The theoretical optical performances of metallic nanoring arrays are calculated based on plasmon hybridization approaches and simulations by Finite Difference Time Domain (FDTD) analysis. Fig 1-1(A) schematically shows a unit cell which is used to represent a typical hexagonal array of nanorings with lattice constant a . The specific nanoring geometries are schematically defined in Fig 1-1(B), where d_o is the outer diameter, t is the ring thickness, and h is the ring height. In this illustration, the cross section of the nanoring is defined to be a semi-circle because it will be more approaching to the practical shapes with regard to the author's work. Depending on the practical situations, other shapes can also be incorporated. In a reported work of Nordlander's group [37], comparisons between nanorings with circular and rectangular cross sectional profiles but with same cross sectional area have been carried out. Similar optical spectra have been obtained despite of the different cross sectional profiles, which indicates minor influences of the cross sectional shapes on the optical behaviors of nanoring arrays.

Fig 1- 1. Schematic illustrations of (A) a unit cell representing a hexagonal array of nanorings, (B) geometrical specifications of a specific nanoring.

The optical behaviors of complex nanostructures can be explained by the plasmon hybridization method established by Nordlander's group in 2003 [38]. In this method, the plasmon resonances of a complicated multi-component structure are expressed in terms of interactions between the plasmon modes of its elementary components. Hence, the plasmon resonances of a nanoring structure can be treated as the hybridized results of the plasmon modes of a nanodisc and a nanohole. The hybridization of the nanohole and nanodisc dipole components will lead to the formation of two discrete plasmon modes, consisting of a low energy bonding mode for the situation when the nanohole and nanodisc have the same polarization direction and a high energy antibonding mode for the case when the two components have opposite polarization directions [39, 40].

Fig 1-2(A) shows the transmission spectrum calculated by Lumerical FDTD Solution for a typical hexagonal array of gold nanorings which is representatively illustrated by the schemes of Fig 1-1. The specifications of the lattice constant and the geometrical parameters are listed in Table 1-1. From the transmission spectrum of this nanoring array, two resonance wavelengths can be observed with the high energy mode located at 556nm and the low energy mode located at 800nm. Fig 1-2(B) and (C) are FDTD simulated charge density distributions at these two respective incident wavelengths. At 556nm, antibonding mode is confirmed by the observation of oppositely aligned dipole orientations of the inner nanohole structure and the outer nanodisc structure. Whereas, bonding mode can be observed at 800nm with the polarized nanohole and nanodisc dipoles aligned in the same direction. Generally, the antibonding mode preserves lower peak intensity since the localized field is weakened due to the opposite alignment. On the other hand, the bonding mode shows higher peak intensity due to the aligned directions of the localized field.

Fig 1- 2. (A) FDTD simulated transmission spectrum of a typical hexagonal gold nanoring array with specifications listed in Table 1-1. (B) & (C) FDTD simulated charge density distributions for this gold nanoring array at (B) antibonding wavelength, (C) bonding wavelength. (Unpublished work by author)

Table 1- 1: Specifications of the lattice constant and the geometrical parameters for a typical hexagonal gold nanoring array discussed by Fig 1-2.

Outer diameter d_o (nm)	Ring thickness t (nm)	Lattice constant a (nm)	Ring height h (nm)
120	40	260	20

In some early studies about the optical properties of nanoring structures, it was found that the resonance wavelengths will be sensitively dependent on the ratio between the ring thickness and the outer diameter (t/d_o) [13, 41]. Fig 1-3 compares the FDTD calculated transmission spectra for hexagonal nanoring arrays with same lattice constant but different nanoring geometries. The corresponding specifications of the lattice constants and the geometrical parameters are provided in Table 1-2. Generally, the thickness of the nanorings and the lattice constant were respectively fixed to be 40nm and 260nm, while the outer diameters were increased from 120nm to 220nm. With reducing value of t/d_o , the bonding mode can be red shifted from visible rang to NIR range with wavelength longer than 1400nm. This can be

interpreted by the enhanced dipolar coupling between the plasmon modes of the inner and outer components of nanoring structures [32, 41]. Theoretically, Aizpurua [13] has deduced the dependence of the bonding frequency on the ratio of t/d_o by the following relationship.

$$\left(\frac{1}{\omega}\right)^2 \propto \epsilon_0 + \epsilon_s \frac{e^{2t/d_o} + 1}{e^{2t/d_o} - 1} \quad \text{Eq(1-1)}$$

where ω represents the bonding frequency, ϵ_0 and ϵ_s correspond to the dielectric functions of the air and substrate, respectively. The relationship illustrated in Eq (1-1) indicates red shift of the bonding mode to a lower frequency with decreased value of t/d_o . Due to the shifting behavior of the bonding mode over such a wide spectrum range covering both the visible and NIR parts, nanoring arrays are treated as attractive candidates for numerous applications in NIR sensing [21, 22, 24, 25, 41-43].

Fig 1- 3. FDTD simulated transmission spectra for hexagonal gold nanoring arrays with different ratios between the ring thickness and the outer diameter (t/d_o). (Unpublished work by author)

Table 1- 2: List of lattice constants and geometrical parameters of the hexagonal gold nanoring arrays for discussions related to Fig 1-3.

Sample array	Outer diameter do (nm)	Ring thickness t (nm)	Lattice constant a (nm)	Ring height h (nm)
1	120	40	260	20
2	160	40	260	20
3	200	40	260	20
4	220	40	260	20

Besides the geometry of each nanostructure, for periodically arranged nanostructures, the optical spectra will be additionally affected by the near field and far field interactions among the nanostructures [44-46]. Near field interaction can be described as the coupling of the electromagnetic fields of closely located adjacent nanostructures. Far field interaction arises from field scattering by the periodically arranged nanostructures. According to a detailed theoretical study by Meier, Wokaun, and Liao [47], they found that strong collective radiation can be resulted due to far field interactions of the periodically arranged nanostructures' dipolar fields when the lattice constant exceeds its critical grating order. Hence, the field interactions of nanostructures are highly dependent on the lattice constants of the periodic arrays [48].

Fig 1-4 is the FDTD calculated transmission spectra for hexagonal gold nanoring arrays with same geometry but different lattice constants. The specifications of the geometrical parameters and the lattice constants are listed in Table 1-3. According to the calculated transmission spectra for lattice constants varying from 160nm to 600nm, it can be observed that the resonance wavelengths can be tuned despite of the fixed nanoring geometry. With the increasing lattice constant from 160nm to 260nm, slight blue shift of the resonance wavelength can be observed. This can be interpreted as weakened near field coupling

between adjacent nanoring structures due to increased spacing [26, 27]. When the lattice constant is further increased, the collective radiation due to far field interactions becomes radiative and starts to show influences on the optical spectra of the nanoring array [25], which is observed as red shift of resonance wavelength with increasing lattice constant.

Fig 1- 4. FDTD simulated transmission spectra for hexagonal gold nanoring arrays with different lattice constants. (Unpublished work by author)

Table 1- 3: Specifications of lattice constants and geometrical parameters of the hexagonal gold nanoring arrays for discussions related to Fig 1-4.

Sample array	Outer diameter do (nm)	Ring thickness t (nm)	Lattice constant a (nm)	Ring height h (nm)
1	120	40	160	20
2	120	40	200	20
3	120	40	260	20
4	120	40	300	20
5	120	40	600	20

In addition, Aizpurua [13] has also studied the effects of the ring height on the optical performances. It was concluded that the field interaction of the top and bottom ring surfaces

will slightly red shift the mode wavelengths. This effect can be neglected by comparing with the dependence of the optical behaviors on the lattice constant and nanoring geometry (ratio between thickness and outer diameter) as discussed in previous paragraphs.

1.3 Motivations

Because of the unique morphologies of nanoring arrays, a large number of technical applications have been explored based on the novel optical, magnetic and electric properties. For metallic nanoring arrays, the excitation of strong LSPRs or the enhancement of electric field has explored plenty of important applications in optical devices [49], chemical or biological sensors [50-53], and metamaterials [54, 55]. On the other hand, for nanoring arrays constructed by magnetic materials, distinctive flux closure states have been observed for iron, nickel or cobalt nanoring arrays, which show the potentials of these magnetic nanoring arrays to be applied for magnetic storage purposes [56-59]. Besides, unique electronic states are exhibited by some nanoring arrays composed of semiconductor materials, such as CdSe, GaN and InGaS, indicating potential applications of semiconductor nanoring arrays as optoelectronic devices [60-62]. Regardless of the materials, the specific behaviors of nanoring arrays can be systematically manipulated by controlling the geometries of each nanoring (ring diameter and thickness) as well as by varying the lattice parameters of the arrays. As indicated by the optical behaviors reviewed in section 1.2, both the nanoring geometries and the lattice constants can significantly determine the optical spectra and the subsequent applications of the corresponding nanoring arrays. Hence, it is vitally important to fabricate large area of nanoring arrays with feasibility to tune both the array spacing and the nanoring geometries.

Among the reported nanofabrication techniques, colloidal nanosphere lithography is regarded as a relative cost effective and high throughput technique to generate nanoring arrays in large areas, although it may not be able to achieve the complexity or precision as a serial of direct writing process such as (E-beam) lithography [53]. Some nanosphere lithography approaches to produce nanoring arrays is through combined ion polishing and electron deposition processes by using non close packed nanosphere monolayers as the templates [32, 63]. Although precise control over the nanoring dimensions can be attained, major challenges to incorporate such approaches arise from the high cost and the delicate fabrication processes. On the other hand, some low cost approaches are based on capillary infiltration, edge spreading or localized dewetting of the patterning materials towards the sites where template nanospheres are located on the substrates [64-67]. These approaches have effectively reduced the cost and simplified the production procedures. However, successful generation of nanoring structures is highly dependent on fine process controls in such as wetting behavior of patterning polymers, flow dynamics and evaporation of filling solvent, and surface properties of template nanospheres. Besides, although the lattice spacing of nanoring arrays can be simply tuned by manipulating the lattice constants of the template nanosphere colloidal crystals, it is still a key challenge encountered by most of current approaches to show flexible control over the nanoring geometries in addition to the control in lattice spacing. Therefore, it is essentially necessary to circumvent the limitations of existing nanofabrication techniques for nanoring arrays by creating a new approach which preserves both easy process control and flexible manipulation of nanoring geometries.

1.4 Objective and Scopes

The overall aim of this thesis is to establish a simple and versatile approach to fabricate nanoring arrays based on a novel perspective of colloidal lithography. This objective will be realized by:

1. Fabrication of 2D polymeric nanosphere monolayer templates

In this study, polymeric nanosphere monolayers were formed on water surface by the spreading effect of ethanol. The nanosphere monolayers were transferred onto desirable substrates and applied as templates for subsequent fabrication of nanoring arrays.

2. Fabrication of nanoring arrays

Nanoring arrays were produced by treating the template polymeric nanosphere monolayers with bridging molecules which can form disordered molecular networks around the contact site of each template nanosphere. The formation of nanoring structures is realized by the physical interpenetration and attractive interaction between the bridging molecular networks and the loosely entangled surface polymer chains of the template nanospheres. It has been demonstrated that the obtained polymer nanoring arrays are capable to be transferred into arrays of gold nanoring structures, despite the transferring approaches are far from optimized.

3. Exploring the versatility of the nanofabrication technique

The versatility of the fabrication method for nanoring arrays has been explored by incorporating various categories of bridging molecules, template nanospheres and supporting substrates. Based on this, systematic analysis about the formation mechanisms of the nanoring structures has been carried out, which establishes the prerequisites for successful

formation of nanoring structures.

4. Manipulating the nanoring morphologies

The dependences of nanoring morphologies on treatment conditions of bridging molecules, dimensions or molecular structures of template nanospheres, and surface properties of substrates have been analyzed accordingly. Besides, both thermal annealing of the template monolayers and vapor annealing of the monolayers with acetone or toluene have been carried out to accelerate the relaxation of the surface polymer chains of the template nanospheres. The nanoring geometries (diameters and volumes) can be manipulated by tailoring the sizes or the annealing processes of the template nanospheres.

1.5 Organization of thesis

This thesis consists of seven chapters and each chapter is briefly summarized as follows:

Chapter 1 provides some background information related to this topic. The optical behaviors and applications of nanoring arrays are briefly reviewed, which consolidates the motivation to establish a fabrication approach for nanoring arrays to overcome the challenges encountered by current fabrication techniques. In the end of this chapter, the main objective and scopes of this thesis are classified.

Chapter 2 compares some common nanofabrication techniques and explains the advantageous of nanosphere lithography over the other techniques. This chapter also reviews some popular methods to produce nanosphere colloidal crystals which can be applied as the

templates in nanosphere lithography. In the end, this chapter discusses about some current nanosphere lithography techniques for fabrication of nanoring arrays.

Chapter 3 shows the original work to fabricate polymeric nanosphere monolayers with a rapid ethanol spreading method. Besides, it also shows the observation of ring shaped footprint arrays by directly peeling off the template nanosphere monolayers due to the relaxation of the surface polymer chains of the template nanospheres.

Chapter 4 demonstrates the fabrication of nanoring arrays by treating the template nanosphere monolayers with bridging molecules. The prerequisites of bridging molecules as well as the effects of treatment conditions are discussed.

Chapter 5 provides a systematic study about the formation mechanisms of the nanoring arrays by incorporating various categories of bridging molecules, template nanospheres and supporting substrates. It explores the versatility of this fabrication technique and establishes the prerequisites for successful formation of nanoring structures.

Chapter 6 exhibits the accelerated nanoring formation by vapor annealing or thermal annealing of the template nanosphere monolayers. It shows the feasibility of this fabrication technique to manipulate the obtained nanoring geometries by tailoring the surface relaxation of the template nanospheres.

Chapter 7 summarizes the important conclusions and major contributions of this thesis work and proposes potential opportunities for future research activities.

CHAPTER 2: Fabrication of Nanoring Arrays – A Review

2.1 Nanofabrication Techniques

Nanofabrication is regarded as a process to generate patterns of nanostructures with controlled geometry, size and spacing. It has become a popular scientific field due to the wide applications contributed by the unique chemical and physical characteristics. These characteristics are determined by the nanostructure morphologies and the arrangement parameters. Some standard lithographic techniques, such as optical lithography, direct-writing, soft lithography and nanosphere lithography, are commonly used in nanofabrication processes to generate nanostructure arrays, including arrays of ring shaped nanostructures.

2.1.1 Optical Lithography

Optical lithography is one of the most widely used techniques to generate patterned features with the assistance of photo-sensitive polymers (photoresists). Extreme ultraviolet (EUV) lithography [68-70] and X-ray lithography [71] are classified as two major types of optical lithography which involve UV radiation and X-ray radiation, respectively, to selectively expose the photoresist through a photomask and transfer the pattern of the photomask into the photoresist by subsequent developing of the exposed photoresist. The pattern created in the photoresist can be further transferred into the underlying substrate by etching process. However, both the UV lithography and X-ray lithography techniques could only provide precise control to microscale dimension rather than to nanoscale range due to the diffraction limit and the constraint to draw nanopatterns on the photomask. Interference lithography [72-

[74] is an improved optical lithography technique which creates periodic patterns on photoresist by coherent interference of the incident light beams. In a standard set-up of the interference lithography system, photomask is not involved, while the periodic pattern is directly created by the interference of the incident laser beam. However, photoresist is still playing a critical role in this technique to transfer the incident pattern. Hence, the capability of the interference lithography technique is still limited by the light sensitivity and etching sharpness of the photoresist [75].

2.1.2 Direct Writing Technique

Direct writing techniques are also playing an important role in emerging applications to provide excellent dimensional control of the created structures down to sub-100nm range. For example, E-beam lithography [76, 77] can directly expose the electron beam to macromolecule polymers which are highly sensitive to electrons and write the nanostructures with desirable geometry and spacing. Compared with the optical lithography, radiation with much shorter wavelength could be achieved by E-beam lithography, leading to higher resolution for the created patterns. FIB technique [78, 79] is based on similar principle as the E-beam process but the radiation source is made up of charged particles instead of electrons. Hole and slot nanostructures can be created in substrates by bombardment of ions. Higher precision in the position of the nanostructures can be achieved by FIB lithography compared with the E-beam lithography due to the better directional etch by the ions with heavier mass compared with the electrons. Nevertheless, the major disadvantages of these direct writing techniques are the low throughput [80, 81] because of the slow writing process and the high cost [82] for the equipment and replacement.

2.1.3 Soft Lithography

Soft lithography [83, 84] is regarded as a powerful and low cost technique to fabricate various large area patterns with controllable spacing and symmetries. A typical process of soft lithography involves the use of a patterned poly(dimethylsiloxane) (PDMS) stamp or mask to print the pattern into another desirable surface. Compared with the optical lithography and direct writing technique, this technique has been widely used to prepare well defined structures with lower requirement in precise positioning but higher demanding for large coverage and inexpensive nanofabrication approaches. The major drawback of this technique is the limited capability in fabrication of certain structures with particular geometries, such as disk-like particles, slit-shaped or circle-liked holes, because of the complex patterning steps as well as some constrains in the molding techniques of the stamps [85].

2.1.4 Nanosphere Lithography

Nanosphere lithography is another cost effective nanofabrication technique for periodic nanostructures besides soft lithography. Compared with the soft lithography technique, it offers a simpler fabrication process but richer types of nanofeatures [9, 23, 86, 87]. The concept of nanosphere lithography was first reported in a work of Fischer and Zingsheim [88], which prepared periodic platinum nanostructures with the assistance of a drop coated monolayer of colloidal nanospheres. Nevertheless, the idea to use colloidal nanosphere assemblies as lithographic masks have not been realized until Deckman and Dunsmuir [89]

reported a preparation process of two-fold mask based on colloidal self-assembly. Subsequently, more and more research works have been started to improve established approaches or to develop new methods with the target to generate colloidal lithographic masks with better quality or nanostructures with more sophisticated geometries for specific applications. There are several typical advantages of nanosphere lithography over other nanofabrication techniques, including faster and simpler preparation process involving few delicate steps, cheaper and larger area fabrication of nanostructures without special apparatus, as well as more flexible fabricating systems due to high material versatility. Therefore, in this thesis work, nanosphere lithography has been selected as a starting component for a novel nanofabrication method of nanoring arrays.

2.2 Fabrication of Nanosphere Colloidal Crystals

As reviewed in previous sections, nanosphere lithography is an attractive technique for nanofabrication because the ordered arrangement of the nanosphere colloidal crystal can be utilized as a lithographic mask to generate well ordered structures. The advantages of this technique are mainly contributed by the ability of the colloidal nanospheres to self assemble into periodic 2D and 3D structures. The 2D structures have especially attracted extensive interest to be applied as lithographic or etch masks. There are a lot of reported approaches to fabricate the template colloidal crystals. Among the variety, several of them are widely accepted due to their ability of long range ordered assembly, such as drop coating method, dip coating deposition, spin coating technique, and assembly at interfaces.

2.2.1 Drop Coating Method

Drop coating is a method to assemble colloidal nanospheres into ordered arrangement through solvent evaporation from a sessile drop of colloidal suspension on a horizontal substrate (as shown in Fig 2-1(A)). The solvent evaporation will induce a directional liquid flow from the interior of the droplet to the edge, which leads to a directional transport of colloidal nanospheres towards the air/liquid/substrate contact line [90]. When the meniscus level at the contact line preserves a height value which is approximately equal to the nanosphere diameter, the nanospheres will be deposited on the substrate along the contact line [91]. Therefore, the accumulation of nanospheres will start from drop periphery, which gives rise to the formation of a ring shaped assembly of colloidal nanospheres. Fig 2-1 (B) is a captured image from a real time study of nanosphere assembly during drop coating process carried out by the author. Multilayer structures are usually generated by this method. To control the number of layers formed, it is essential to finely control the evaporation rate of the solvent, concentration of the suspension, and size of the droplet [92, 93].

Fig 2- 1. (A) Schematic view of colloidal nanosphere assembly in a sessile drop on a horizontal substrate. (B) A captured image from a real time study of nanosphere assembly in drop coating process (unpublished work by author).

2.2.2 Dip Coating Deposition

Dip coating is another assembly method based on the capillary flow of colloidal particles towards the air/liquid/substrate contact line and the compressive effect of the meniscus [91, 94, 95]. Different from the horizontal drop coating technique, as shown in Fig 2-2 (A), it is a vertical deposition method in which the contact line is moving downwards steadily with respect to the vertically positioned substrate. This could be achieved either by lifting up the substrate with a step motor or by removing the suspension with a pump (in our case as shown in Fig 2-2(B)).

Fig 2- 2. (A) Schematic view of colloidal nanosphere assembly by vertical deposition. (B) Photograph of the set-up for dip coating deposition, which involves the assistance of a pump to remove the suspension (original work from the author). (C) Photographic image and (D) Cross sectional FESEM image of colloidal crystals obtained by dip coating method (unpublished work by author).

Large area of multilayer structures can be obtained by this method. The number of layers could be uniform over a large coverage range provided a steady movement of the contact line or the substrate. Fig 2-2(C) and (D) are the photographic and FESEM images, respectively, of 3D colloidal crystals generated in one of our dip coating works. 2D colloidal monolayer is also possible to be obtained with this vertical deposition technique. However, similar as the

drop coating method, to tailor the arranged pattern, it requires specific control on the detailed processing parameters for this technique, especially on the velocity of the contact line movement and the concentration of the colloidal suspension [96, 97].

2.2.3 Spin Coating Technique

Spin coating is a commonly used approach to prepare 2D colloidal crystal [98-102]. As illustrated in Fig 2-3, the colloidal suspension with adjusted viscosity is deposited on a substrate mounted on the rotary stage of a spin coater. Subsequently, the solvent will flow away upon the spinning of the stage, which reduces the thickness of the deposited suspension. Over the substrate surface in spinning movement, the deposited liquid will preserve a decreased thickness from the peripheral region towards the central region. Similar as the drop coating mechanism, when the height of the suspension in the central region approaches the size of colloidal nanoparticles, the nanoparticles will protrude from the liquid layer with ordered arrangement. The quality of the obtained crystal is highly dependent on the surface treatments for both of the colloidal nanoparticles and the substrate [103]. Besides, to control the final structures, specific attentions should also be arranged to the adjustment of spin speed and even the substrate surface area.

Fig 2- 3. Schematic view of colloidal nanosphere assembly by spin coating technique.

2.2.4 Assembly at Interfaces

Another common method for the fabrication of 2D colloidal crystal is by assembly of nanospheres at liquid/vapor or liquid/liquid interfaces [104-106], as illustrated in Fig 2-4. The nanospheres are either directly introduced to the interface or adsorbed from one of the subphases to the interface by certain adjusted driving forces. Once the nanospheres are adsorbed at the interface, a monolayer of self-organized colloidal crystal could be formed due to the attractive interaction among the floating nanoparticles. This method offers high throughput for the generation of 2D colloidal crystals and the monolayer can be simply transferred to a desirable substrate with a wide range of materials. Hence, in this thesis work, the 2D template colloidal crystals have been fabricated based on this method. More detailed discussion about this assembly technique will be provided in next chapter.

Fig 2- 4. Assembly of nanospheres into 2D colloidal crystal at interface.

2.3 Fabrication of Nanoring Arrays by Nanosphere Lithography

For decades, colloidal crystals have been applied in nanofabrications of various functional nanostructure arrays through well designed routes [107, 108]. The most conventional route is to generate arrays of nanotriangles or nanodots by etching and deposition processes through the interstices of a colloidal crystal mask[28]. Tailored arrangement of nanostructures can be achieved by tilted or rotated deposition [50-52]. By further manipulating the colloidal masks with post treatments of RIE milling or thermal annealing, the shape of the colloidal

nanoparticles can be tailored, which results in arrays of functional nanostructures with tuned feature shapes [8, 49, 55]. Meanwhile, besides triangular or dot features, colloidal crystals have also been employed as template scaffolds to generate other functional patterns, such as nanohole and nanoring structures [30, 54, 109]. Especially for the nanoring arrays, because of the potential applications in optical sensing [110-112], high resolution imaging [113], as well as magnetic storage [114], well ordered nanoring arrays have recently achieved significant interest in the research world.

For nanofabrication of periodic arrays of ring shaped nanostructures, besides the nanosphere lithography, there are a number of other reported fabrication routes, such as the top down techniques involving electron beam lithography [115] or optical lithography [114, 116], the bottom up approaches through porous templates [117] or block copolymer self-organization [118-124], and some other routes based on the dewetting mechanisms on patterns generated by micro contact printing [125-127] or breathe figure technique [128]. However, due to the simplicity, versatility and cost efficiency of nanosphere lithography compared with other nanofabrication techniques, nanosphere lithography is a more popular approach for the production of nanoring arrays on large length scale. In the rest part of this section, a review of some common nanosphere lithographic routes to create arrays of nanoring features will be provided.

2.3.1 Ion Polishing and Electron Deposition

A conventional route to fabricate nanoring arrays is through ion polishing and electron deposition by using a 2D colloidal crystal as the mask. Most of the fabricating approaches in this area have involved the transformation of the close packed 2D nanosphere monolayers

into non close packed nanofabrication masks by ion milling or chemical etching. As shown in Fig 2-5(A), target material was deposited onto the interstitial areas of a non close packed mask. By subsequent reactive ion etching (RIE) of the deposited layer with the non close packed nanospheres as the etching masks, ring shaped nanostructures could be obtained around the contact sites [63, 108, 111]. Alternatively, each nanosphere itself can be turned into nanoring structure by selective ion etching. As illustrated in Fig 2-5(B), passivative material could be deposited into the interstices of the non close packed nanospheres with the top portion of each nanosphere protruding the passivation layer. Then the structure was applied with directional ion etching to selectively remove the unpassivated volume of each nanosphere, and finally the passivated portion of each nanosphere constituted to a ring shaped nanostructure embedded inside the passivation layer [129].

Both of the approaches illustrated by Fig 2-5(A) and Fig 2-5(B) are based on the anisotropic ion etching of target materials for the final nanoring structures. Another type of fabrication approach in this area is based on electron deposition of target material into ring shaped grooves created by manipulating the template nanosphere monolayer [130]. A typical approach is schematically illustrated in Fig 2-5(C). Firstly, non close packed array of nanopillars was obtained by etching and heat treatment of a close packed 2D nanosphere template. Then a layer of template material was deposited onto the interstitial areas. Subsequently, ring shaped grooves can be achieved by secondary etching of the non close packed template nanopillars [131]. Alternatively, the nanopillars were replaced with deposition of another layer of template materials, groove structures can be obtained by fine control in the post deposition treatment of the template materials [32]. Finally, target material was deposited into the ring shaped groove structures, and arrays of nanoring features can be obtained.

Fig 2- 5. (A) Fabrication of nanoring array by etching the target material with the non close packed nanospheres as the etching mask. (B) Fabrication of nanoring structures by etching the non close packed template nanospheres which are passivated by a passivative layer deposited in the interstitial regions. (C) Nanoring array formed by electron deposition of target material inside the ring shaped groove structures created by manipulating the template 2D nanosphere monolayer.

Well defined nanoring structures can be achieved by such fabrication routes. Nevertheless, as mentioned above, most of these approaches are restricted to 2D masks with non close packed nanostructures, which results in more challenges in the fabrication process. Besides, the ion polishing or electron deposition technique will always require delicate facilities and processing environment, which increases the cost and further constrains the capability to adopt such fabrication processes.

2.3.2 Capillary and Edge Spreading Infiltration

On the other hand, nanoring array can be generated through localized infiltration of target materials or target precursors around the contact site [62, 64, 65, 132-138]. Fig 2-6(A) represents a typical route for this type of approach. First, a template colloidal crystal was immersed in a patterning suspension of target materials or target precursors. Both the surface properties of the template colloidal crystal and the substrate were carefully manipulated before usage, so that the patterning suspension will prefer to locally accumulate around the contact sites upon subsequent evaporation or heat treatment. Hence, nanorings can be formed at the contact sites after precipitation of the target materials or after reduction of the target precursors. Some reported alternative approaches were based on localized infiltration of template agents which subsequently induced accumulation of target materials by eletroless plating [139, 140]. Besides, Cremer's group [141] has reported a fabrication method which was based on similar localized accumulation mechanisms as this type of approach. However, in their work, no external patterning material was added into the fabrication system. Instead, the patterning solutes were generated by partially dissolving the polymeric substrate with well designed solvent.

Alternatively, instead of infiltrating patterning solutes through evaporation or heat treatment of the suspension phase, patterning solutes can also be infiltrated by an edge spreading approach [66, 142] illustrated in Fig 2-6(B). Typically, polar solution of alkanethiols is applied to ink a planar stamp which is subsequently placed on top of a 2D non close packed nanosphere monolayer. All the surfaces of the stamp, nanospheres and the substrate should be inert to the alkanethiol solution, which induces guided reactive spreading of the self assembled monolayer (SAM) formed by the alkanethiols. With the inked stamp serving as a

reservoir, the patterning molecules can diffuse along the nanosphere surfaces to the substrate where ring shaped patterns can be formed due to the lateral expansion of the diffused SAMs.

Fig 2- 6. (A) Fabrication of nanoring arrays by localized capillary infiltration of target solutes through evaporation or heat treatment of the patterning suspension. (B) Generation of nanoring structures by infiltration of target molecules through guided reactive edge spreading of the molecules along the template nanosphere surfaces.

Compared with the physical fabrication processes based on ion polishing or electron deposition, such infiltration techniques have significantly reduced the requirements and costs of the fabrication process. However, a major challenge for localized infiltration is to tune the interactions among all the components in each fabrication system so as to achieve fine control about the coating preference of the target solutes. In addition, successful localized infiltration of the target solutes will be highly dependent on the dynamic flow of the patterning suspension, which induces additional challenges for this type of technique.

2.3.3 Localized Dewetting

Another method for fabrication of nanoring arrays which has been widely used in relative

research field is based on localized dewetting of polymer films [31, 67, 143-145]. As illustrated in Fig 2-7, such approach is based on a similar technique as micro contact printing. A typical fabrication process would start with the modification of substrate surfaces with layers of hybrid polymer films containing target materials. Then, a sandwich structure is generated by assembly of close packed colloidal crystal in between two parallel substrates through a vertical deposition approach. Subsequently, the sandwich structure is annealed at a temperature above the glass transition temperature of the polymer films, which would imprint the hard template nanospheres into the polymer films. Meanwhile, upon annealing at a temperature above the glass transition temperature, the polymer films with well designed viscosity and thickness would become unstable, which induces rupture and dewetting of the polymer films on the substrate. Hence, nanoring structures could be obtained due to the dewetting of the polymer films towards the contact sites of the template nanospheres.

Fig 2- 7. Formation of nanoring arrays by localized dewetting of polymer films based on a micro contact printing approach.

Compared with the infiltration method reviewed above, such a process based on micro contact printing technique has easier process control by avoiding the challenges to manipulate the properties of various surfaces or to control the flow dynamics of patterning suspension. Nevertheless, successful generation of nanoring structures will be highly dependent on the well designed thermal behaviors of the hybrid polymer films. Besides, the

capability of such fabrication method will also be restricted by the fabrication of the sandwich structures. Last but not least, it will be a key challenge for such approaches to attain the tunability of nanoring dimensions.

CHAPTER 3: Ring Shaped Footprint Arrays from 2D Polymeric Colloidal Crystals

This chapter will elaborate the formation of nanoring footprint arrays from 2D colloidal crystals. 2D polymeric nanosphere monolayers were fabricated by directly spreading the nanospheres onto a water/air interface by using ethanol as the spreading medium. In this process, the monolayers are formed at the interface mainly based on the contributions from the spreading behavior of ethanol and the self-assembly behavior of the floating nanospheres. After the monolayers were deposited on desirable substrates, due to the swelling behavior and thermal motion of the tangling polymer chains along each template nanosphere, ring shaped footprints will be formed around the contact site due to localized accumulation of these polymer chains.

3.1 Fabrication of Polymeric Nanosphere Monolayers by Rapid Ethanol Spreading

Some common fabrication methods for colloidal monolayers which are currently applied in various research areas are the approaches based on vertical deposition [96] or spin coating [103]. The vertical deposition process is a time consuming approach since a slow and steady movement of the meniscus is required to preserve the ordering and uniform coverage for the deposited colloidal film. This method is effective for the growth of 3D colloidal crystals, but faces significant challenges for monolayer deposition. The spin coating method is more popular for monolayer fabrication since large scale monolayers can be obtained within much shorter time duration. However, it requires redispersion of the nanospheres into specific solvents. Besides, the capability of this approach would be limited by the low feasibility in

mass production.

In this study, monolayers of polymeric nanospheres are prepared by a modified rapid ethanol spreading method based on a reported self-assembly process from the research group in Tsinghua University [146]. This method has been proven to be a robust way to produce monolayers of hydrophobic nanoparticles in large area. It is a fast, simple, and flexible process since the entire fabrication procedure could be accomplished within minutes and the generated monolayer could be transferred to any flat substrate. Besides, this method can also be applied to produce monolayers with more complex structures by involving multiple types of nanoparticles.

3.1.1 Synthesis of Polymeric Colloidal Nanospheres

Water based monodispersed polymeric nanospheres are prepared by emulsion polymerization in nitrogen atmosphere, either with emulsifier or without emulsifier. For polymerization processes with emulsifier, monomers are firstly added into deionized water to an extent which is much higher than its solubility. This leads to a dispersion of monomer droplets in water. Then, Sodium Dodecyl Sulfate (SDS) is applied as the surfactant (emulsifier). SDS molecules will position along the interface between monomer droplets and water, which reduces the surface tension of the droplets and stabilizes the droplets. In this thesis work, all the emulsifier assisted polymerizations have used SDS with concentrations below the Critical Micelle Concentration (CMC, 0.0082M in water at room temperature). For such processes, the polymerization mechanism is mainly based on precipitation of oligomeric radicals [147-149]. Generally, upon subsequent addition of water soluble initiators, radicals generated in the water phase initiate the solute monomers to form oligomeric radicals. The oligomeric

radicals will precipitate from the water phase after reaching critical chain lengths, which leads to the formation of stable primary latex particles or the coagulation with previously-formed primary particles. Since the overall surface area of the particles is much greater than that of the larger and fewer monomer droplets, the initiators will typically react in the particles but not in the droplets. Hence, monomers in the droplets will diffuse through the water phase to the polymerizing particles until eventually the droplets disappear and all the monomers have been fed to the particles. During this process, some SDS molecules will locate along the surface of the particles, which provides an adequate surface potential to ensure colloidal stability. In the end, water based polymeric nanospheres are achieved as spherical clusters of polymer chains. Negatively or positively charged nanospheres are respectively obtained by using sulfate- or amidine- initiators.

On the other hand, to eliminate the influences of the surfactant molecules, some of the polymeric nanospheres involved in this thesis were prepared by an emulsifier free polymerization method. For such processes, the polymerization mechanism is similar as the one described above, except that no emulsifier is applied [150, 151]. Generally, the reaction of the solute monomers with the initiating radicals leads to the generation of surface active oligomeric radicals in the water phase. These oligomeric radicals grow, associate and form primary particles which are further swollen by the residual monomers. However, without emulsifier, the small primary particles will keep coagulating into large particles until an adequate electrostatic potential energy is achieved to stabilize the growing particles. This induces additional challenges in process control and size manipulation. Therefore, in this thesis work, the majority of the polymeric nanospheres were synthesized by emulsifier assisted polymerization.

3.1.2 Preparing Monolayers of Polymeric Nanospheres

The procedure for the ethanol spreading method is illustrated in Fig 3-1(A). First, the as-synthesized polymer nanosphere suspension is cleaned with deionized water by repeated centrifugation for at least two times. Then the cleaned nanosphere suspension is mixed with absolute ethanol (99.9%, Merck) in volume ratio of 1:1. Upon slow injection of the nanosphere suspension onto a water surface, the nanospheres would rapidly spread and simultaneously form ordered close packed monolayer domains floating on the water surface. Subsequently, the monolayer can be transferred to a desired substrate and dried in ambient atmosphere. Fig 3-1(B) shows a monolayer of PS nanospheres with diameter of 260nm floating on the water surface in a petri dish before transferring to substrates. The resplendent color indicates a long range ordering of the nanosphere assembly. Fig 3-1(C) and Fig 3-1(D) are FESEM images of the top view and the side view of the monolayer transferred onto a silica substrate, respectively.

In this fabrication method, ethanol plays a significant role due to its specific behavior at the water/air interface. Ethanol is characterized as a weak amphiphilic molecule since it contains both hydrocarbon (hydrophobic) group and hydroxide (hydrophilic) group. There will be a strong tendency for amphiphilic molecules to adsorb at the water/air interface to lower the surface free energy. Therefore, when ethanol approaches to a water surface, it will be thermodynamically favored for ethanol molecules to adsorb at the water/air interface with the hydrocarbon groups aligning towards the air phase while the hydroxide groups bond to the water phase. However, such adsorption will also be opposed by the entropy loss due to localized adsorption of molecules at the interface. Since ethanol is miscible with water, it will interact with the water/air interface in a way to preserve the balance between reducing the

surface free energy by adsorbing at the interface and increasing the entropy by mixing with the water phase or evaporating to the air phase.

Fig 3- 1. (A) Procedure to fabricate monolayers of polymer nanospheres by rapid ethanol spreading. (B) A monolayer of 260nm PS nanospheres floating on the water surface before transferring to substrates. Top view (C) and side view (D) FESEM images of the monolayer transferred onto a silica substrate.

The surface tension of ethanol (22 mN m^{-1}) is much lower than that of water (72 mN m^{-1}). Hence, a solution of water/ethanol mixture will preserve lower surface tension compared with a pure water solution. Higher ethanol concentration in the mixture will give rise to lower surface tension of the mixture solution. According to the Marangoni effects [152], a surface

tension gradient will naturally lead to mass transfer from the lower surface tension region to the region with higher surface tension. Therefore, in this fabrication process for nanosphere monolayers, when the nanosphere suspension mixed with certain amount of ethanol is brought to the water surface, a hydrodynamic spreading of the nanospheres along the water surface will result due to the surface tension gradient. Simultaneously, the spreading ethanol molecules will mix with the water subphase or evaporate into the air phase to increase the entropy of the system.

Fig 3-2 shows the spreading of PS nanospheres on water surface for dispersions with various ethanol concentrations, with overall concentration of nanospheres in the mixtures kept constant at 1wt%. When the dispersing solvent contains 100% ethanol as shown in Fig 3-2(A), there will be large difference between the surface tensions of the dispersed solvent and the water subphase, leading to rapid and turbulent spreading of the nanospheres on the water surface. Since the flow is not stable, it will be difficult for the floating nanospheres to assemble into long range ordered domains.

Fig 3-2(B) and Fig 3-2(C) are photographs for the spreading of nanospheres dispersed in mixtures of 80% ethanol/20% water and 50% ethanol/50% water, respectively. It can be observed that, as the ethanol concentration is reduced from 100% to 80% and 50%, the flow becomes more stable at lower concentration of ethanol, and nanospheres can assemble into larger area of ordered domains (observed as the resplendent color) due to more stable spreading.

However, when the ethanol concentration is further reduced from 50% to 20% (Fig 3-2(D)), the surface tension gradient between the dispersion solution and the water subphase will be very low, which cannot induce significant rapid spreading of nanospheres on the water

surface. Instead, the mixing of the dispersion solution into the water subphase will become dominant. Hence, it can be observed that most of the nanospheres are brought into the water subphase while very few of them remain spread at the surface.

Fig 3- 2. Photographic images of nanospheres spreading on water/air interface by dispersing the PS nanospheres in water/ethanol mixtures at ethanol fraction of (A) 100%, (B) 80%, (C) 50%, and (D) 20%.

After the polymeric nanospheres are pinned to the water surface by the spreading of ethanol, since the surface of a nanosphere is hydrophobic, it becomes a stable state for the nanospheres to float and stay on the water/air interface. Due to the buoyancy and particle weight, the shape of the water/air interface will be somewhat perturbed. According to some reported works ^[153-155], ethanol addition could result in reduction of nanoparticle surface

charge density in the aqueous solution, which effectively reduces the electrostatic repulsion between neighboring particles making it possible for the particles to approach closer to each other. When two similar particles are sufficiently close to each other, perturbations of the water surface caused by these two particles will overlap (as shown in Fig 3-3), which induces a lateral capillary force between the particles [156]. Such capillary force will bring the floating particles to close pack with each other to lower surface free energy by reducing the deformation in the interface shape as well as to lower the gravitational potential energy by decreasing the interparticle distance. Therefore, upon a stable spreading of nanospheres on the water surface, the colloidal nanospheres will cluster with each other to form monolayer of ordered domains floating on the water surface.

Fig 3- 3. Deformation in the shape of the water/air interface caused by the buoyancy and particle weight.

3.2 Formation of Ring Shaped Footprints through Localized Accumulation of Nanosphere Surface Molecules

The surface of a polymeric nanosphere is not a smooth and solid surface but is a soft interface constructed by entangled polymer chains [157, 158]. At the interface between the nanosphere and the surrounding solvent, there will be two counterbalancing forces[159]. One is the swelling force due to osmotic contribution ($\Delta\bar{F}_{m1}$) to expand the polymer chains by diffusion of solvent molecules. Another one is the restraining force due to interfacial energy

contribution ($\Delta\bar{F}_t$) to reduce the total area of interface. Hence, at the equilibrium state between the nanosphere and the environmental solvent, the following relationship exists:

$$\Delta\bar{F}_t + \Delta\bar{F}_{m1} = 0 \quad \text{Eq(4 – 1)}$$

The contribution of partial free energy can be related to the interfacial free energy (γ) as:

$$\Delta\bar{F}_t = 4\pi r^2 d\gamma \quad \text{Eq(4 – 2)}$$

where r stands for the radius of the nanosphere, and $d\gamma$ is the change of the interfacial free energy. According to Eq (4-1) and Eq (4-2), a decrease in interfacial free energy will give rise to a negative restraining force and a positive swelling force, which results in expansion of the polymer chains at the nanosphere surface to equilibrate the interface.

The polymeric nanospheres involved in this study were synthesized through polymerization methods by using deionized water as the final dispersion medium for the as-synthesized nanospheres. Due to the polar nature of water molecules and hydrophobic nature of most hydrocarbon chains, it usually preserves a high value for the interfacial free energy between a polymeric nanosphere and surrounding water solvent. Thus, each as-synthesized nanosphere could be treated as a spherical cluster of polymer chains which are compactly entangled with each other. After the polymeric nanospheres are deposited onto desirable substrates as a monolayer and transferred from the water solvent to the air environment with lower polarity, the interfacial free energy between the polymer chains and the environment will be reduced. Hence, the polymer chains at the nanosphere surface will start to expand towards the air phase and relax to a more loosely packed status.

To lower the total interfacial energy, it is thermodynamically favored to reduce the total

interfacial area around the contact site where an individual nanosphere is touching the substrate. This drives expanded surface chains to fill up the gap between the nanosphere surface and substrate by localized accumulation around the contact site. Such accumulation is proposed to be achieved by random thermal motion of expanded polymer molecules during the relaxation process. In the region close to the contact site, some expanded surface molecules will touch the substrate surface due to molecular chain stretching. This establishes bridges for some other molecules from neighboring regions to reach the substrate surface. By storing the nanosphere monolayer in ambient environment for a period of time, some expanded polymer chains from the nanosphere surface will be able to accumulate around the contact site, reducing the total interfacial area. Upon physically peeling off the template nanospheres, the accumulated polymer chains will remain adsorbed on the substrate so as to reduce the surface energy of the substrate.

Fig 3-4(A) and Fig 3-4(B) are, respectively, the 3D and 2D AFM images of a sample after removing a 260nm PS nanosphere monolayer from a silica substrate. The PS nanospheres were synthesized with initiators consisting of negatively charged sulfate groups, and the monolayer has been stored for 2 weeks in ambient before usage. The monolayer was simply removed by peeling off with a thermal tape. (It is recommended to store the thermal tape in dry ambient to avoid tape remnants which result in contaminations and noise on the desired patterns) Once a nanosphere was peeled off, some of the accumulated molecular chains around the contact site would be left over, resulting in a ring shaped remnant footprint. This can be supported by the illustration in Fig 3-4(C), which compares the measured cross section profile of a footprint with a drawn circle in same diameter as the template nanosphere (260nm). It can be observed that the inner edge of the ring shaped remnant matches very well with the circular outline.

Fig 3- 4. (A) 3D view and (B) 2D view of the ring shaped footprint left over on silica substrate after peeling off a 260nm PS nanosphere monolayer, (C) The cross section profile of a remnant ring(red, measured) matches with a 260nm circular nanosphere outline(white, drawn). The scale bar is 100nm.

3.3 Chapter Summary

To conclude, by making use of the thermodynamic behavior of ethanol at the water/air interface, 2D colloidal crystals have been formed on the interfaces. By maintaining the ethanol concentration in the water/ethanol mixture to be around 50%, the surface tension of the mixture could be manipulated to achieve a stable spreading of nanospheres on water/air interface. It was found that high concentration of ethanol in the mixture will give rise to large surface tension gradient, which results in a rapid and turbulent spreading and hinders the

assembly of floating nanospheres into ordered domains. However, a low concentration of ethanol in the mixture will not be able to induce a dominant spreading effect compared with the mixing effect due to small surface tension gradient, and the nanospheres will be brought into the water subphase rather than spreading on the interface.

Arrays of nanosized ring shaped footprints can be fabricated from templating monolayers of polymer nanospheres. Due to reduced interfacial free energy between the environment and the surface polymer chains, the polymer chains along the surface of each nanosphere will relax to more loosely packed entanglement when stored in air. To reduce the total interfacial energy around the contact site, some expanded surface chains which are close to the substrate can accumulate around the contact site through random thermal motions upon relaxation, which forms a ring shaped footprint for each template nanosphere.

CHAPTER 4: Forming Nanoring Arrays with Assistance of Bridging Molecules

As reviewed in Chapter 2, among the variety of fabrication approaches for nanoring arrays, colloidal crystal lithography is regarded as a relatively simple and cost efficient technique. However, most of the reported nanosphere lithographic approaches would still be constrained by the requirement of fine control in the fabrication process or by the lack of flexibility in manipulating the final morphologies. This thesis introduces a novel and simple patterning method to prepare nanoring arrays by nanosphere lithography based on the footprint observation as introduced in Chapter 3 [160]. In this method, the template monolayer is treated with molecules which can form molecular networks on the substrate surfaces. Such molecular networks can interpenetrate and actively interact with the expanded tangling polymer chains along the surface of template nanospheres, which enhances the adsorption of the surface polymer molecules onto the substrate. Since the treatment molecules are acting as bridges to bring additional surface polymer chains to adsorb onto the substrate surface, these molecules are named as ‘bridging molecules’ in this thesis work. With the assistance of bridging molecules, arrays of well defined nanoring features can be prepared on various substrates through enhanced localized adsorption of molecular chains from the template nanosphere surface. Since the bridging molecules are the only external additives which do not require any specific control in handling, an easy process control could be preserved by this method. In addition, Chapter 5 and Chapter 6 will show the manipulation of the nanoring morphologies by varying the fabrication process, which indicates the versatility and flexibility of this approach.

(3-Aminopropyl) triethoxysilane (APTES) is well known for its fast hydrolysis and easy condensation on substrate with hydroxyl surface groups, forming a disordered molecular network on the substrate surface through inter and intra reactions among the functional groups. Hence, most of the treatments for template monolayers in this thesis work will be demonstrated by applying APTES as the bridging molecule. This chapter will introduce the approach to generate nanoring arrays with the assistance of APTES treatment, as well as an analysis on the prerequisites for molecules to show bridging effects. In the end, by analyzing the coating behaviors of APTES molecules on silica surfaces, the effects of APTES treatment conditions on nanoring morphologies will be discussed.

4.1 Fabricating Nanoring Arrays with Assistance of APTES Treatment

The basic procedure to prepare nanoring arrays is schematically illustrated in Fig 4-1. As described in section 3.1 of Chapter 3, polymeric nanosphere monolayers were prepared by the method of rapid ethanol spreading and stored in the ambient atmosphere for certain time duration to allow sufficient thermal motions of the surface chains (Fig 4-1(A)). Then, APTES treatments of monolayers were carried out by immersing the as-prepared monolayers in ethanol solution of APTES molecules. After the treatment, the monolayers were continuously rinsed with ethanol to remove any remaining unbonded free APTES molecules, and subsequently dried in atmosphere (Fig 4-1(B)). Finally, after peeling off the templating nanospheres, arrays of nanosized ring features could be obtained on the substrates as illustrated in Fig 4-1(C).

Fig 4- 1. Basic procedure to generate an array of nanorings. (A) Nanosphere monolayer stored in atmosphere after fabrication, and the surface molecules relax during storage. (B) APTES treatment applied to the monolayer to improve the final ring features. (C) Nanoring array obtained after peeling off the monolayer template.

In this thesis, APTES was used as the bridging molecule in most of the treatments before peeling off the monolayer from substrates with hydroxyl surface groups. As shown in Fig 4-2(A), each APTES molecule contains one amino group and three ethoxysilane groups. Upon exposure to water molecules, APTES will go through hydrolysis reactions [161], in which the ethoxysilane groups will react with water molecules to form Si-OH groups and release ethanol molecules. A typical hydrolysis reaction is illustrated in Fig 4-2(B).

Fig 4- 2. (A) Chemical structure of an APTES molecule. (B) A typical hydrolysis reaction of one APTES molecule with three water molecules.

APTES molecules can interact with the hydroxyl groups on a substrate surface through 2 major types of bonding [162], including covalent bonding to form siloxane bonds by reactions between the Si-OH groups and the hydroxyl groups (Fig 4-3(A)), and hydrogen bonding between the hydroxyl groups with the amino groups or with the Si-OH groups (Fig 4-3(B)). Besides, polymers can be created through horizontal polymerization (Fig 4-3(C)) which forms siloxane bonds among the surface attached APTES molecules, or through vertical polymerization (Fig 4-3(D)) which involves attachment of APTES molecules from solution to those surface bounded molecules [163]. In addition, cyclic reaction (Fig 4-3(E)) mainly through hydrogen bonding could also take place in an individual bonded APTES molecule, or between a bonded molecule with the substrate surface, or between two neighboring bonded molecules [164].

As discussed above, APTES can interact with the hydroxyl functionalized substrate or with each other in a number of ways. Without specific control, all of these reactions will take place in a single coating process. Due to these inter and intra interactions among the functional groups of APTES molecules and the hydroxyl groups on the substrate surface, disordered 3D molecular networks with multilayer cross linked structures would be usually obtained after APTES molecules are coated on hydroxyl functionalized surfaces.

Fig 4- 3. (A) Covalent bonding and (B) hydrogen bonding between the functional groups of APTES molecules and the hydroxyl groups on substrate surface. (C) Horizontal polymerization among surface bonded APTES molecules. (D) Vertical polymerization among the molecules in solution with the surface bonded molecules. (E) Cyclic reactions occurred for APTES molecules coated on substrate surface.

The bridging effect of APTES molecules is to enhance the adsorption of polymer molecules from the template nanosphere surface onto the substrate. Such effect can be mainly attributed to the anchoring of loosely packed surface chains by the APTES molecular network formed through inter and intra interaction among the functional groups. Due to the interpenetration between the APTES network and the surface polymer chains around the contact region, upon peeling off the nanospheres, some extra surface molecules will be anchored on the substrate

in addition to the accumulated ones. Besides, attractive interactions can also be induced between the amino groups of bonded APTES with the electron rich PS chains as well as with the negatively charged sulfate end groups introduced during the nanosphere synthesis. For template nanospheres constructed by electron rich polymer chains, such induced attractive electrostatic interaction can also contribute to the bridging effect of APTES.

Fig 4-4(A) and Fig 4-4(B) are respectively the 3D and 2D AFM images of nanoring array generated on silica substrate with APTES treatment. After 2 week storage, before peeling off, a monolayer of 260nm PS nanospheres on silica substrate was treated with 1vol% APTES in ethanol solution at room temperature for 1 hr. Compared with the footprint array shown in Fig 3-4 which was generated without APTES treatment, it could be found that the nanorings prepared with APTES treatment are more uniform, distinct and complete.

Fig 4- 4. (A) 3D and (B) 2D view of the nanorings obtained by a 260nm PS nanosphere monolayer on silica substrate after 1 hr treatment in ethanol solution of 1vol% APTES.

As shown in Fig 4-5, by comparing the nanoring cross section profiles, it can be observed that APTES treatment will give rise to ring morphology with increased diameter and height. In this study, the ring diameter is defined as the measured space between the two peaks from

the nanoring cross section profile. The measured diameter and height of the ring shaped remnants prepared without APTES treatment were around 55nm and 1.5nm, respectively, while the diameter and height of the nanorings generated after treatment were measured to be around 80nm and 3.5nm respectively.

Fig 4- 5. Cross section profiles of nanorings on silica substrates templated by 260nm PS nanosphere monolayers (A) without (B) with APTES treatment before peeling off the nanospheres.

The nanoring arrays generated with APTES treatment have also been characterized by Fourier Transform Infrared Spectroscopy (FTIR). The characterization was carried out with the reflection mode of a HYPERION 3000 FTIR Microscope. Cleaned silica surface was applied for the background scan. Fig 4-6 shows the FTIR absorption spectrum of a typical nanoring sample. Despite of the weak signal to noise ratio due to the small values of nanoring height, the FTIR spectrum indicates the presence of polystyrene by showing the peaks around wavenumber 1100 and 3000. The peak around wavenumber 1100 is related to the in-plane bending of the conjugated aromatic CH bonds, and the one around wavenumber 3000 is contributed by the stretching of such CH bonds. Besides, in the fingerprint region of the

FTIR spectrum, the two peaks around wavenumber 700 are also well matched with the absorption from the out-of-plane bending of the benzene ring and the aromatic CH bonds.

Fig 4- 6. FTIR absorption spectrum of a nanoring sample prepared with APTES treatment.

It is proposed that the nanoring formation after treatment is mainly due to the effect of bridging molecules rather than the contribution from the effects of solvent (absolute ethanol). To clarify this, after storage for 2 weeks, a 260nm PS nanosphere monolayer was treated in pure solvent (absolute ethanol) without bridging molecules at room temperature for 1 hr. The 3D and 2D AFM images of the nanorings prepared after such treatment are shown in Fig 4-7(A) and Fig 4-7(B), respectively. Little improvement could be observed for the nanoring morphology by comparing with the one prepared without ethanol treatment (Fig 3-4).

Fig 4- 7. (A) 3D and (B) 2D AFM images of a nanoring array on silica substrate generated by a monolayer of 260nm PS nanospheres after 1 hr treatment in absolute ethanol.

Therefore, the localized accumulation of polymer chains around the contact site is mainly through the anchoring effect by the bridging networks. Although the swelling of the surface polymers may be slightly enhanced by moving the polymeric nanospheres from atmospheric environment to ethanol solvent, it can be deduced that the short treatment duration (1hr) is not sufficient to allow extra accumulation of swollen surface molecules through the slow thermal motion. Besides, it can also be deduced that the transportation of individual polymers through the solvent phase is not significant. Thus, the major path for molecular motion is along the template nanosphere surface, which explains the reason for the generation of ring shaped morphologies.

4.2 Prerequisites for Bridging Molecules

Bridging molecules can act as a ‘bridge’ to enhance the adsorption of surface polymer chains on the substrate. The mechanism for adsorption enhancement is proposed to be contributed

from the anchoring of loosely entangled surface chains by a bridging molecular network as well as from the attractive interaction between bridging molecules and the polymer chains. Due to the amino groups and the hydrolyzed ethoxysilane groups, APTES can be qualified as a good candidate to provide the bridging effect in such fabrication process of nanorings. Besides APTES, other molecules, which are capable to provide similar chemical behaviors by their functional groups, can also be applied as bridging molecules for the formation of nanorings.

Take 3-mercaptopropyl trimethoxysilane (MPTMS) as an example, as shown in Fig 4-8(A). Each MPTMS molecule consists of a thiol group and 3 methoxy groups. Besides the ability to bond with the hydroxyl groups on substrate surface, the hydrolyzed methoxy groups can also interact with each other as well as with the thiol groups. Therefore, a disordered network can be formed on the substrate surface, which can interpenetrate with the loosely packed polymer chains from the nanosphere surface, providing the anchoring effect similar to the APTES network. Fig 4-8(B) and (C) are, respectively, the 2D and 3D AFM images of a nanoring array on silica substrate formed by a 260nm PS monolayer which has been stored for 2 weeks and subsequently treated with ethanol solution of 1vol% MPTMS at room temperature for 1 hr before removing the template nanospheres.

This study has also carried out some other treatments involving cysteamine molecules for PS monolayer on gold substrate or OTMS molecules for PS monolayer on silica substrate. The molecular structures of these two types of molecules are illustrated in Fig 4-8(A), which indicates that both of them can preserve attractive interactions with the polymer chains and the substrates. However, each cysteamine molecule contains only two functional groups, which cannot afford the formation of molecular network. For OTMS molecules, it is also

difficult to form molecular networks due to the long alkylene tails, although each molecule contains 3 silane groups which provides the potential to form molecular network. After peeling off the templating nanospheres with the same storage and treatment histories as those fabrication systems mentioned above, no distinct ring shaped remnants could be observed. This indicates that the improvement in ring morphology is mainly due to the physical anchoring mechanism, although the attractive interactions of bridging molecules with the polymer chains or the substrate could also provide some minor contribution.

Fig 4- 8. (A) Molecular structures of MPTMS, Cysteamine and OTMS. (B) 2D and (C) 3D view of the nanorings on silica substrate obtained by a monolayer of 260nm PS nanospheres after treatment in ethanol solution of 1vol% MPTMS for 1 hr.

Therefore, besides the requirement to actively interact with both of the polymer chains and the substrate, a major prerequisite for potential bridging molecules is that the functional groups of the molecules should be able to perform inter and intra interactions to form a

molecular network on the substrate. To achieve this, each molecule has to contain at least 3 interactive functional groups which can react with each other. Besides, it is advised to avoid selection of molecules with all the functional groups bonded at a single site, like OTMS, because the volume of the molecular tail may hinder the effective formation of a molecular network. In addition, moderate chain length among the functional groups is preferred for candidate molecules. Either an over-dense or over-loose network structure may lead to reduced interpenetrating or anchoring effects.

4.3 Influences of APTES Treatment Conditions

4.3.1 Coating Dynamics of APTES on Silica Surfaces

Before studying the influences of treatment conditions, it is crucial to know the coating behaviors of APTES on substrates with hydroxyl groups. In this section, the coating dynamics will be studied by measuring the contact angles of water droplets and the attachment morphologies of negatively charged gold nanoparticle on silica substrates after various APTES treatments. Before treatment, all the silica substrates were cleaned with piranha solution (3:1 volume ratio of sulfuric acid and hydrogen peroxide) for 1 hr at 90°C. Then the substrates were rinsed with deionized water, blow dried with nitrogen gas, and stored in ambient atmosphere for subsequent treatment. The treatments were carried out by immersing the silica substrates in ethanol solution of APTES at room temperature.

When the substrates were stored in a humid atmosphere (the humidity in Singapore can be as high as 90%), water layer will be adsorbed on the substrate surface. It has been well studied and proven that, upon exposure of free APTES molecules, one monolayer of water on the

substrate surface will be sufficient to fully hydrolyze the adsorbed APTES molecules, eventually forming a thin film of cross-linked siloxane network at the interface [165, 166]. In the case of silica substrate, the amino groups of APTES molecules can effectively interact with the silica surface. Hence, the adsorbed water molecules will be effectively displaced and become free to hydrolyze the ethoxysilane groups of APTES. Meanwhile, the amino groups can also weaken the OH bonds of the silanols in the hydrolyzed APTES molecules or on the substrate surface, which enhances the condensation to form siloxane bonds.

As shown in Fig 4-9, generally, APTES coating will increase the contact angle due to the increased surface roughness and the attachment of hydrocarbon molecules on the hydrophilic polar silica surface. It could be observed that regardless of the treatment concentration, the contact angles will approach a stable value if sufficient treatment duration was provided. Such stabilized contact angle indicates a uniform and stabilized molecular structure coated on the substrate surface. Besides, it was found that treatment with higher APTES concentration will give rise to faster increment in contact angles, thus contact angle values would be stabilized in shorter time. This could be explained by the faster coating process due to larger amount of free molecules available in the region nearby the substrate surface. By comparing treatments of 1% APTES with those of 10% APTES, the contact angles will approach to a similar stabilized value after treatment duration of 50min, which indicates complete coverage of APTES coating with similar molecular structures could be achieved on the substrate surfaces after treating for 50min, despite the variation in treatment concentrations. However, if the treatment concentration is as low as 0.1%, although long treatment duration of 300min (5hr) was provided, the contact angle will not be able to achieve a value which is close to those obtained by treatment with higher concentration (1% or 10%). This is proposed to be caused by the lack of molecules at such low concentration to form a similar stabilized

molecular structure as those with higher concentrations.

Fig 4- 9. Measured contact angles of water droplets on silica substrates after APTES treatments with various concentrations for time durations until 300min.

According to the discussion for the contact angles represented in Fig 4-9, it could be deduced that treatment with duration of 60min would be sufficient for the all the 3 treating systems (0.1%, 1% and 10%) to generate stabilized APTES molecular structures coating on the substrates surfaces. Therefore, to study the forming dynamics of the molecular structures, Fig 4-10 shows the more detailed graphs for the contact angles obtained within 60min for the treatment systems mentioned above. Meanwhile, morphologies of negatively charged gold nanoparticles attached on substrates after treatments of 1% APTES for different time durations have been recorded and presented in Fig 4-11. Since the amount of negatively charged gold nanoparticles adsorbed on the substrate is mainly determined by the coverage density of the positively charged amino groups on the substrate surface, it is reasonable that, by studying the contact angles (Fig 4-10) together with the nanoparticle attachment (Fig 4-

11), a clearer view could be achieved about the structure change of the APTES coating from the beginning of treatment until the formation of stabilized structure (60min).

The hydrosol of citrate stabilized gold nanoparticles with average diameter of 15nm was obtained using a reported synthesis approach [167, 168]. Before usage, the gold nanoparticle hydrosol was cleaned by centrifuging and redispersion in deionized water. The citrate stabilized gold nanoparticles will preserve negative surface charges with a measured zeta potential value of -44.4 ± 8.36 mV (measurement conducted by Malvern Nanosizer). The adsorption of gold nanoparticles was carried out by immersing the treated substrates in water solution of gold nanoparticles with concentration of 10^{12} particles / ml.

Fig 4- 10. Contact angles of water droplets on silica substrates after treatments with various APTES concentrations for time duration within 60min.

Fig 4- 11. FESEM images of gold nanoparticles adsorbing on silica substrates with treatment of 1% APTES for time duration of (A) 2 min, (B) 5 min, (C) 10 min, (D) 20 min, and (E) 60 min. The scale bars are 100 nm.

Although all of the inter and intra interactions among APTES functional groups and the substrate surface are possible to take place in a single coating process, it is proposed that in the very beginning of the coating process, isolated molecules will be first adsorbed on the substrate before significant cyclic or polymerizing reactions take place. Fig 4-11(A) shows gold nanoparticles adsorbed on a substrate with 2min treatment of 1% APTES. It could be deduced that the adsorbing and packing of isolated molecules on the substrate surface is a rapid process, thus within time duration of as short as 2min, the coverage density of unbonded amino groups would be already sufficient to attract large number of nanoparticles.

Upon an increase in treatment time, when the neighboring bonded molecules are sufficiently close to each other due to increased packing density of the APTES molecules, cyclic reactions and horizontal polymerization of the bonded molecules would become more significant. This will reduce the polar contribution from substrate as well as reduce the

density of exposed amino and silanol groups, which results in larger contact angles and fewer adsorbed gold nanoparticles. As shown in Fig 4-11(B), when the duration of 1% APTES treatment is increased to 5min, lower coverage density of unbonded amino groups would be resulted due to the cyclic reactions among the attached APTES molecules, thus fewer gold nanoparticles could be adsorbed on the substrate.

When the treatment time is further increased, the effect of vertical polymerization to attach molecules on top of the first molecular layer will start to become as significant as the cyclic reaction and horizontal polymerization of the first layer, which introduces extra unbonded amino and silanol groups to the substrate surface. This enhances the polarity of the surface and reduces the value of contact angle. Take the 1% APTES treatment as an example, when the treatment time is increased from 5min to 10 min, as shown in Fig 4-10, a decrease in contact angle could be observed. Due to the more complete cyclic reactions among the first layer of attached molecules, although vertical polymerization could provide a few unbonded amino groups, the overall coverage density of unbonded amino groups could be reduced for treatment of 10min compared with the one of 5min. Therefore, as shown in Fig 4-11(C), the amount of gold nanoparticles adsorbed on substrate surface was reduced by increasing the treatment time from 5min to 10min.

With longer treatment duration, more molecules could be attached by vertical polymerization, which increases the overall density of unbonded amino groups, resulting in larger number of nanoparticles adsorbed on the substrate (as shown in Fig 4-11(D) for treatment of 20min). At the same time, horizontal polymerization and cyclic reactions would also take place among the attached molecules, which results in the formation of a multilayer cross linked structure. This increases the surface roughness and also reduces the influence of the polar silica surface

on the contact angle formation, thus the value of contact angle keeps increasing for treatment duration from 10min to 20min, as indicated by the graph for 1% APTES treatment in Fig 4-10.

By further increasing the treatment time from 20min to 60min, a balance could be achieved among the vertical polymerization to contribute unbonded polar functional groups, the horizontal polymerization to reduce the polar contribution of substrate, and the cyclic reaction to reduce the unbonded polar groups. Such balance results in stabilized contact angle (Fig 4-10) as well as stabilized densities of silanol groups and unbonded amino groups (Fig 4-11(E)) after treatment of 1% APTES with time duration of 60min.

Therefore, it is proposed that coating of APTES molecules on silica substrate, in our specific case, could be treated as a 2-step process. The first step mainly involves the rapid attachment of isolated molecules and the subsequent cyclic and polymerizing reactions of these attached molecules. In the first step, the dominant structure formed on the substrate surface will be a molecular monolayer since the contribution from vertical polymerization is not significant. The second step is a compromised process among vertical polymerization, horizontal polymerization and cyclic reaction. Vertical polymerization will introduce extra polar groups to the surface, which reduces the contact angle. Nevertheless, cyclic reaction and horizontal polymerization will consume polar groups and cross link the molecules, which increases the contact angle. The compromise among these reactions explains the fluctuation in the contact angle graph at the beginning of the second step, regardless of the treatment concentration (as shown in Fig 4-10). In the end of the second step, a balance could be reached among the various reactions, which leads to the formation of a multilayer cross linked network with stabilized contact angle and stabilized density of unbonded polar groups. Therefore, by

referring to such coating dynamics of APTES molecules, the conditions for a stable molecular coating can be achieved, which facilitates the process development for APTES assisted fabrication of nanoring arrays.

4.3.2 Influences on Nanoring Morphologies by Treatment Conditions of APTES Molecules

Fig 4-12 shows the effects of APTES treatment time on the nanoring morphologies at 1 vol% treatment concentration. It was found that fast treatment for period as short as 10 min (Fig 4-12(A)) could already lead to formation of nanorings with comparable dimensions as those generated with longer treatment for periods of, eg. 1 hr (Fig 4-12(B)) and 3 hr (Fig 4-12(C)). Such immediate impact of APTES treatment is due to the rapid formation of the molecular network. As discussed in section 4.3.1, with treatment duration of 10min, vertical polymerization could occur to attach APTES molecules on top of the first attached layer. Meanwhile, the structure should be sufficiently cross linked at that time due to the cyclic reactions and horizontal polymerization of the attached molecules. However, compared with the nanorings prepared by treatment of longer time, the morphologies of those prepared by 10min treatment are not complete in shape and uniform in height. This is because the APTES network would be uniformly coated on the substrate surface only if sufficient time duration (at least 50min for 1 vol% treatment as indicated by Fig 4-9 and Fig 4-10) is provided for it to achieve a stabilized multilayer structure.

Upon increase in treatment time, better defined nanoring features could be achieved, with increment in both the height and width of the ring walls, as indicated by the comparison of the cross section profiles of the nanorings in Fig 4-12 (D). This is because longer treatment time can result in molecular network composed of more layers. In other words, a thicker network can be formed if longer treatment duration is provided, which can interact with

larger surface area of expanded polymer chains around the contact region of the template nanosphere. Therefore, after peeling off the template nanosphere, more polymer molecules could be anchored which results in remnant nanorings with larger values of height and diameter.

Fig 4- 12. 3D AFM images of nanorings on silica substrate generated by 260nm PS nanosphere monolayers after treatment with 1vol% APTES in ethanol solution for (A) 10 min, (B) 1hr, and (C) 3hr. (D) Comparison among the cross section profiles of nanorings generated with APTES treatment of various time durations.

The final nanoring morphologies would also be dependent on the concentration of bridging molecules during the treatment. Treatment with higher concentration of bridging molecule will lead to faster attachment of the bridging molecules onto the substrate, which allows the formation of stable and uniform network structure in shorter time. Fig 4-13(A) and Fig 4-13(B) are nanoring arrays formed after 10 min treatment in ethanol solution of APTES with concentration of 1vol% and 10vol%, respectively. Rings with complete shape and uniform

height could be obtained by treatment with a high concentration of APTES (10vol%), although the treatment time is as short as 10 min. This is consistent with the contact angle study shown in Fig 4-10. For a 10min treatment with 10vol% APTES, the contact angle could achieve a stabilized value, which indicates the formation of a uniform multilayer network over the substrate surface.

Fig 4- 13. 3D AFM images of nanorings on silica substrate generated by 260nm PS nanosphere monolayer after 10min treatment with ethanol solution of APTES in concentration of (A) 1% and (B) 10%.

For 1hr treatment of APTES in ethanol solvent, the change in nanoring features generated by systems with increasing concentration of APTES could be observed from Fig 4-14(A) (1vol%), Fig 4-14(B) (10vol%) and Fig 4-14(C) (15vol%). The treatment duration of 1 hr is sufficient for all these 3 systems to achieve a uniform structure. However, since higher concentration of bridging molecules could lead to faster attachment of molecules onto the substrate, a thick network could be formed, which anchors larger amount of polymer chains onto the substrate. The change in the nanoring dimensions could be directly observed from Fig 4-14(D), which compares the cross section profiles of the nanorings prepared with treatment of the three different concentrations. The average heights of the nanosized rings were accordingly increased from 3.5nm (1vol%) to 5.5nm (10vol%) and 7.5nm (15vol%).

Fig 4- 14. 3D AFM images of nanoring arrays on silica substrate generated by 260nm PS nanosphere monolayers after 1hr treatment with ethanol solution of APTES in concentration of (A) 1%, (B) 10%, and (C) 15%. (D) Comparison among the cross section profiles of nanorings generated with APTES treatment of various concentrations.

4.4 Chapter Summary

In summary, the coating behavior of APTES on substrate surfaces with hydroxyl groups can be generally treated as a 2-step process. A single molecular layer is formed during the first step through attachment of isolated APTES molecules followed by subsequent cyclic and horizontal polymerizing reactions, while the vertical polymerization is insignificant in this step. The second step is for the formation of multilayer structures once the vertical polymerization is as significant as other reactions. Provided sufficient time for coating, multilayer network with stabilized density of unbonded functional groups would be achieved.

APTES can act as a bridging molecule to enhance the localized molecular accumulation of surface chains, so as to obtain nanorings with better defined features. The bridging effect of APTES is mainly attributed to its specific coating behaviors. Due to inter and intra interactions among the functional groups of APTES molecules and the hydroxyl groups, a disordered molecular network will be formed on the substrate, which anchors loosely entangled polymer chains by interpenetration and results in more polymer molecules accumulated around the contact site. Formation of distinct nanoring features is mainly contributed by this anchoring effect.

Some other molecules besides APTES could also be applied as bridging molecules. In addition to the requirement of active interactions with both of the substrate and the polymer chains, a major prerequisite for potential bridging molecules is that each molecule has to contain at least 3 mutual interactive functional groups to ensure the formation of a molecular network on the substrate.

CHAPTER 5: Nanoring Fabrication in Alternative Systems

In this chapter, to elaborate the versatility and feasibility of the bridging molecule assisted fabrication technique as introduced in Chapter 4, formation of nanoring structures have been demonstrated by applying alternative fabrication systems which consist of different template nanospheres or other supporting substrates. Based on alternative template nanospheres and substrate surfaces, a comprehensive study about the specific effects of these two components on the nanoring formation and morphologies will be provided, so that clearer understanding about the ring formation mechanisms could be achieved in addition to the effects of bridging molecule treatment as discussed in Chapter 4. In the end of this chapter, the author will also demonstrate the potential to transfer the polymeric nanoring arrays into nanoring patterns composed of other functional materials.

5.1 Nanoring Formation by Alternative Template Nanospheres

As discussed in Chapter 4, PS nanospheres can be treated as spherical clusters of tangling PS chains. Along each PS chain, there are a large number of electron rich benzene groups with stable conjugated structures. Hence, these PS chains can only interact weakly with the amino groups of the bonded APTES molecules. Thus, for template nanospheres composed of PS chains, the remnant rings are mainly formed by anchoring of the expanded PS chains with bridging molecular network, while the interaction between the bridging molecules with the PS chains only showed minor effects on the nanoring formation.

An alternative monolayer system has been established involving 280nm template nanospheres consisting of PMMA chains. After storage for 2 weeks in air and a subsequent standard bridging molecule treatment, nanorings with morphologies as shown in Fig 5-1(A) and Fig 5-1(B) have been obtained on silica substrate. Similar to PS chains, the entangled PMMA chains will also expand during storage and be anchored around the contact sites through interpenetration with the APTES molecular network. However, compared with the PS chains, the PMMA chains will preserve stronger attractive interaction with the bonded APTES molecules due to the active interaction between the carboxyl groups along PMMA chains and the hydrolyzed ethoxysilane groups of APTES molecules. As a result of such active interaction between polymer chains and bonded bridging molecules, it provides another significant effect on nanoring formation in addition of the contribution from the anchoring effect. Therefore, more remnant molecules can be accumulated around the contact sites. As shown by the cross section profile in Fig 5-1(C), the diameter and height of a PMMA nanoring obtained by a 280nm PMMA nanosphere are respectively around 105nm and 10nm. Both of these values are larger than those obtained by PS template nanospheres with similar diameter (260nm), which were measured to be around 80nm and 3.5nm, respectively.

Fig 5- 1. (A) 2D AFM image, (B) 3D AFM image and (C) cross section profile of nanorings on silica substrate templated by a monolayer of 280nm PMMA nanospheres, the monolayer was treated with 1% APTES in ethanol solution at room temperature for 1 hr. The scale bar in the inset is 100nm.

Besides, monolayers of silica nanospheres have also been applied with the same storage history and treatment conditions as the PMMA monolayer. Silica powders with diameter of 500nm were purchased from Alfa Aesar and used as received. 2.5 wt% of silica powders were dispersed in ethanol/water mixture (1:1 ethanol / deionized water) and assembled into monolayers with the rapid ethanol spreading method. The FESEM image in Fig 5-2(A) shows the morphology of a template silica nanosphere monolayer. Different from the PS or PMMA nanospheres which are constructed by large number of tangling thermoplastic chains, each silica nanosphere can be regarded as a dense network constructed by silica-oxygen bonds, which will not be capable to provide surface chains to interact with the bridging

molecular network. After peeling off the treated template monolayers of silica nanospheres, no distinct nanoring remnants could be observed (Fig 5-2(B)). This further supports the claim that the nanoring structures are constructed by adsorbed polymer chains from each template nanosphere surface, while the bridging molecular network formed around the contact site will not be able to form observable ring-shaped remnant structure due to short treatment time.

Fig 5- 2. (A) FESEM image of a template silica nanosphere monolayer. (B) AFM image of the remnants on silica substrate templated by a monolayer of 320nm silica nanospheres after treatment in ethanol solution of 1vol% APTES for 1 hr.

According to the analysis in this section, a prerequisite for template nanospheres can be concluded: that is the nanosphere should comprise polymer chains which can further contribute to construct the remnant nanostructures with the assistance from bridging molecules. The nanoring morphologies will be affected by the strength of interaction between the bridging molecules and the relaxed polymer chains along the surface of each template nanosphere. This interacting strength is mainly dependent on two aspects: (1) the anchoring effects due to interpenetration of the tangling polymer chains and the bridging molecular networks and (2) the attractive interaction between the functional groups along each polymer chain and the ones present in each bridging molecule. For template nanospheres with stable

functional groups along the polymer chains, like the benzene groups along PS chains, aspect (2) shows insignificant contribution. Thus, the nanoring formation by such template nanospheres will be mainly determined by the aspect (1). This point is consistent with the observation and discussion for PS template nanospheres in section 4.2 of Chapter 4. On the other hand, for template nanospheres containing functional groups which can actively interact with the bridging molecules, such as the carboxyl groups of PMMA, both aspects can contribute significantly, resulting in distinct and improved nanoring structures.

5.2 Effects of Template Nanospheres on Nanoring Formation

5.2.1 Geometrical Dependence on Template Nanosphere Size

The periodicity of nanoring array is dependent on the periodicity of the template nanospheres. Figure 5-3 shows the AFM images of nanoring arrays on silica substrate generated by treating the PS monolayers with a standard bridging molecule treatment (ethanol solution of 1% APTES for 1 hr at room temperature). The diameters of the PS nanospheres are respectively 165nm (Fig 5-3(A)), 260nm (Fig 5-3(B)), and 600nm (Fig 5-3(C)). All the monolayers were stored for 2 weeks before usage. To facilitate the analysis of the dependence of the nanoring dimensions on the template nanosphere size, the side view of the remnant morphology before peeling off the nanosphere and the top view of the remnant after peeling off the nanosphere are schematically illustrated in Fig 5-3(D).

Fig 5- 3. Nanoring arrays on silica substrate templated by PS nanospheres in diameter of (A) 165nm, (B) 260nm and (C) 600nm. The scale bars in the insets are 100nm. (D) Schematic illustrations for the side view of the remnant morphology before a template nanosphere was peeled off and the top view of the remnant after the template nanosphere was peeled off. (E) The measured nanoring diameters are plotted as a function of the square root of the diameters of the template nanospheres.

To study the geometrical relationship between the ring-shaped remnants and the template nanospheres, two major assumptions have been made to simplify the discussion. The first assumption is to treat the polymeric nanosphere to be an ideal solid sphere, which establishes the dependence of the remnant diameter (d) on the diameter (D) of template nanosphere and the maximum height (h) of the accumulated polymer chains as the following relationship:

$$d = 2\sqrt{h(D - h)} \approx 2\sqrt{Dh} \rightarrow d \propto \sqrt{Dh} \quad \text{Eq (5 - 1)}$$

The second assumption is that not all the polymer chains over the whole surface of a template nanosphere can be effective in contributing to the total accumulated volume around the contact site. It is proposed that only the relaxed surface molecules within distance (H) from the substrate are able to reach the substrate surface. The value of H is dependent on the interacting strength between the substrate and the surface molecules upon peeling off of the template nanosphere. Therefore, the accumulated volume (V) of a nanoring is determined by the partial surface area (S) for the portion of the template nanosphere which is defined by the distance H from the surface of the substrate.

$$S = \pi DH \quad \& \quad V = \frac{\pi}{8} h (d_o^2 - d_i^2) \rightarrow d_o^2 - d_i^2 \propto \frac{DH}{h} \quad \text{Eq (5 - 2)}$$

where d_i and d_o are, respectively, the inner and outer diameter of the remnant ring. The diameter (d) of a remnant ring can be approximately related to the values of d_o and d_i as follows:

$$d \approx \frac{d_o + d_i}{2} \quad \& \quad d_o^2 \gg d_i^2 \rightarrow d_o^2 - d_i^2 \sim 4d^2 \quad \text{Eq (5 - 3)}$$

Therefore, the following relationship can be derived from Eq (5-2) and Eq(5-3):

$$d \propto \sqrt{\frac{DH}{h}} \quad \text{Eq (5 - 4)}$$

According to Eq (5-1) and Eq (5-4), the geometrical effect of the template nanosphere size (D) on the diameter of the remnant ring (d) can be expressed by the Eq (5-5) listed below.

$$d \propto \sqrt[4]{H}\sqrt{D} \quad \text{Eq (5 - 5)}$$

H can be treated as a constant for template nanosphere monolayers with the same storage condition and the same bridging molecule treatment history. In this case, the nanoring diameter (d) is linearly related to the square root value of the template nanosphere diameter ($\sqrt{D}$). As shown in Fig 5-3(E), such linear relationship could also be evidenced by the graphical plot of the measured ring diameters (d) at respective square root values of the corresponding nanosphere sizes ($\sqrt{D}$).

Meanwhile, higher value of H could be achieved either by enhanced relaxation of the nanosphere surface molecules or by enhanced interaction of the relaxed molecules with the substrate by bridging molecule treatment. Therefore, provided the same value for the size of template nanospheres (D), according to Eq(5-5), larger ring diameters (d) could result from treatment of bridging molecules. This is consistent with the observation from Fig 4-5 that nanorings with larger diameter have been obtained from a 260nm nanosphere monolayer after APTES treatment compared with those generated with the same template monolayer but without treatment.

Nevertheless, for the average height of a remnant ring, a larger value should be measured compared with the applied value (h) involved in the calculation above. After treating with bridging molecules, the polymer chains along the nanosphere surface nearby the contact

region would interpenetrate with the molecular network formed by the bridging molecules and, at the same time, also entangled with neighboring polymer chains. As a result, upon peeling off the template nanosphere, extra neighboring polymer chains beyond the defined effective region could also be anchored, leading to larger values of measured height and volume.

Fig 5- 4. 3D AFM images of nanoring arrays on silica substrate generated after 1hr treatment with ethanol solution of 1% APTES by monolayers of PS nanosphere in diameters of (A) 165nm, (B) 260nm and (C) 600nm.

Due to this factor, it would be practically difficult to precisely derive the geometrical dependence of the nanoring height or volume on the size of the template nanosphere. Instead, only a general statement could be made about this relationship, which is that nanorings with higher values of height and volume could be obtained by using larger template nanospheres due to larger effective surface area. This can be experimentally observed from the 3D images for the nanorings generated by template nanospheres with diameter of 165nm (Fig 5-4(A)),

260nm (Fig 5-4(B)), and 600nm (Fig 5-4(C)). In addition, same as the height and volume, the measure value of nanoring diameter (d) might also be slightly shifted because of the factor that extra remnants would be presented, but the linear relationship between d and $\sqrt{D}$ is still generally true according to the fitted graph shown in Fig 5-3(E).

5.2.2 Stabilizing Surfactant Molecules Introduced During Nanosphere Synthesis

As discussed in section 3.1.1 of Chapter 3, the template polymeric nanospheres were synthesized through polymerization of monomers and stabilization by surfactant molecules (SDS). Although excessive SDS molecules in the nanosphere suspension have been removed by the cleaning steps before the suspension was applied to fabricate nanosphere monolayer, some SDS molecules may still be adsorbed along the surface of the nanospheres. For template nanospheres coated with surfactant molecules, due to the amphiphilic properties, the surfactant molecules would prefer to adsorb through random walk to the substrate/air or the substrate/nanosphere interface, rather than to stay at the nanosphere/air interface. Besides, it is true that the small surfactant molecules would be more mobile than the entangled long polymer chains. Therefore, the surfactant molecules could accumulate around the contact site even before the surface polymer chains reach there. As a result, the remnant rings obtained after peeling off the template nanospheres would be constructed by both of the anchored polymer chains and the accumulated surfactant molecules.

However, since the surfactant molecules are much smaller than the long polymer chains, it is proposed that the ring shaped remnant volumes are mainly constructed by the long surface chains from the polymeric nanosphere surfaces, while the small surfactant molecules left on the nanosphere surfaces could only introduce minor influences on the nanoring volumes. To

clarify this, a comparable nanoring fabrication process has been carried out by using template monolayers of 370nm PS nanospheres which were synthesized without the involvement of any surfactant molecules.

Similar to the monolayer templates involved in previous discussion, these monolayers of 370nm PS nanospheres without surfactant molecules were deposited on silica substrates and stored in ambient atmosphere for 2 weeks to allow expansion of the surface polymer chains. Without treatment of bridging molecules, a template monolayer was directly peeled off, and the remnant morphologies are shown in Fig 5-5. It was found that ring shaped remnants could still be obtained although there was no surfactant molecule present along the surfaces of the template nanospheres. Hence, these ring shaped footprints are purely constructed by the long surface chains.

Fig 5- 5. (A) 2D and (B) 3D AFM images of the ring shaped footprints left over on silica substrate after directly peeling off a template monolayer of 370nm PS nanospheres without surfactant molecules.

Monolayer of 370nm PS nanospheres without surfactant molecules, after stored for 2 weeks, has also been applied with a standard bridging molecule treatment. After peeling off the treated monolayer, a nanoring array can be obtained as shown in Fig 5-6(A) and Fig 5-6(B).

The cross section profile of a remnant ring is shown in Fig 5-6(C), from which the ring diameter could be observed to be around 105nm. Besides, another 3 more data points for nanoring diameters have been measured and fitted into the graph of Fig 5-3(E) with regard to this template nanosphere size (370nm). As indicated by Fig 5-6(D), it can be observed that the measured ring diameters for template monolayer of 370nm nanospheres without surfactant molecules fitted quite well with the linear plot. This further validates the linear dependence of the nanoring diameters on the square root of the template nanosphere diameter. In addition, it also indicates the insignificant effect of the surfactant molecules on the formation of nanorings or on the morphologies of generated nanorings, which proves the statement that the nanorings are mainly constructed by the large polymer chains from the template nanosphere surfaces.

Fig 5- 6. (A) 2D AFM image, (B) 3D AFM image and (C) cross section profile of nanorings on silica substrate templated by a monolayer of 370nm PS nanospheres without surfactant molecules, the monolayer was treated with 1% APTES in ethanol solution at room temperature for 1 hr. The scale bar in the inset is 100nm. (D) The measured values of nanoring diameters with regard to 370nm template PS nanospheres without surfactant molecules were fitted into the graph of Fig 5-3(E).

5.2.3 Charged End Groups of Polymer Chains Introduced During Nanosphere Synthesis

Besides stabilizing surfactant molecules, as discussed in section 3.1.1 of Chapter 3, negatively charged sulfate end groups have been introduced to polymer chains as initiators during the nanosphere synthesis process. According to the study provided in section 4.2 which discussed about the prerequisites for bridging molecules, for template monolayers of PS nanospheres, ring shaped remnants are formed mainly through the interpenetration between PS chains and the bridging molecular networks rather than through the attractive electrostatic interaction between bridging molecules and PS chains. In addition, an ideal PS chain is a macromolecule constructed by a large number of styrene monomer units ending with only two end groups, giving rise to sparse distribution of charged end groups over the volume of the nanosphere. Therefore, it is proposed that charged end groups of polymer chains would only have minor effect on the formation of nanorings.

To clarify the effects of charged end groups, a monolayer of positively charged 340nm PS nanospheres has been deposited on silica substrate and stored in air for 2 weeks, followed by subsequent standard bridging molecule treatment. These PS nanospheres were synthesized by using amidine groups instead of sulfate groups as initiators, thus the end groups of each PS chains will be positively charged. After peeling off the treated monolayer, as shown in Fig 5-7(A) and Fig 5-7(B), an array of ring shaped remnants could still be generated, despite of the repulsive electrostatic interactions between the amino groups of APTES molecules and the positively charged end groups of the PS chains. This indicates the insignificant effect of the charged end groups of polymer chains on nanoring formation.

Fig 5- 7. (A) 2D AFM image, (B) 3D AFM image and (C) cross section profile of nanorings on silica substrate templated by a monolayer of 340nm positively charged PS nanospheres, the monolayer was treated with 1% APTES in ethanol solution at room temperature for 1 hr. The scale bar in the inset is 100nm. (D) The measured values of nanoring diameters with regard to 340nm positively charged template PS nanospheres were fitted into the graph of Fig 5-3(E).

Fig 5-7(C) is the cross section profile of a nanoring templated by one of the positive PS nanospheres, from which a ring diameter around 90nm could be observed. By fitting the measured diameters into the graph of Fig 5-3(E), it is found that the measured diameters for these 340nm positive template nanospheres are lower than the expected value, as shown in Fig 5-7(D). This can be explained by the reduced interactive distance (H) due to the repulsive interaction between the amino groups of APTES molecules and the positively charged end groups of the polymer chains. Meanwhile, a slightly higher value of ring height could be observed from Fig 5-7(C) by comparing with the one obtained from 370nm template PS nanospheres without surfactant molecules (Fig 5-6(C)). Since the end groups of the polymer

chains are positively charged, the adsorption of polymer chains on negatively charged substrate before APTES treatment will be enhanced. Hence, although a lower value of ring diameter would result due to the reduced H value during APTES treatment, the final ring height could achieve a higher value due to the enhanced adsorption of polymer chains before treatment.

5.3 Fabrication of Nanoring Arrays on Alternative Substrates

All of the template monolayers for nanoring generation mentioned above are deposited on silica substrates. To demonstrate the versatility of this fabrication method, alternative fabrication systems have been established by involving monolayers of 260nm PS nanospheres deposited on polycarbonate (PC) or gold substrates. Similar as the template monolayers applied in other systems, these monolayer samples were stored in air for 2 weeks before usage.

Fig 5-8 shows the ring shaped remnant morphologies formed on PC substrates without (Fig 5-8(A&B)) and with (Fig 5-8(C&D)) subsequent standard bridging molecule treatment before peeling off the template monolayers. For the nanostructures generated on PC substrate by directly removing the template monolayer (Fig 5-8(A)), more distinct and complete ring shaped morphologies can be observed comparing with the ring remnants generated on silica substrate through the same fabricating processes (Fig 4-5(A)). According to the cross section profile (Fig 5-8(B)), the ring diameter and height are respectively around 90nm and 5nm, both of which are higher than those of the remnant on silica substrate. Compared with hydrophilic silica substrate surface, the PC substrate surface will show higher affinity with

the PS chains due to hydrophobic interaction. This enhances the accumulation of relaxed polymer chains onto the substrate surface, leaving larger amount of polymers adsorbed around the contact sites after removing the template nanospheres. As a result, better defined remnant nanostructures can be obtained.

Fig 5- 8. 3D AFM images and cross section profiles for nanoring structures generated on polycarbonate substrates (A, B) without and (C, D) with bridging molecule treatment before removing the templated monolayers of 260nm PS monolayers. All these monolayers were stored in air for 2 weeks before usage, and the bridging molecule treatment was carried out with ethanol solution of 1% APTES for 1hr at room temperature. The scale bars in the insets are 100nm.

For the nanoring formed on PC substrate with the assistance of a standard bridging molecule treatment, as shown by the cross section profile in Fig 5-8(D), the values of the ring diameter and height are around 100nm and 8nm, respectively. Both of these values are increased compared with those for the one without treatment (Fig 5-8(B)). Since the treatment solvent will not significantly affect the remnant morphologies as discussed in Chapter 4, such enhancement in remnant accumulation is proposed to be caused by the bridging effect of

APTES molecules. Polycarbonate is a thermoplastic polymer composed of carbonate groups ($-\text{O}-(\text{C}=\text{O})-\text{O}-$). The hydrolyzed ethoxysilane groups of APTES molecules can actively interact with the carbonate groups. Hence, similar to the coating behavior on silica substrate, a disordered APTES molecular network can also be formed on the surface of PC substrate, which improves the nanoring morphology by anchoring the expanded tangling polymer chains along the template nanosphere surface.

Beside semiconductor (silica) and polymer (PC) substrates, this nanofabrication technique can also be applied to form nanoring structures on metallic substrates. In this thesis, gold surfaces were prepared by evaporating 20nm gold layers on silica substrates. Before deposition of nanosphere monolayers, all the gold surfaces have been cleaned with acetone, followed by rinsing with absolute ethanol. Then, the cleaned gold surfaces have been rinsed with deionized water and finally stored in water for subsequent monolayer deposition. The monolayers have been stored in air for 2 weeks and subsequently applied with standard bridging molecule treatments before peeling off.

According to the reported work of Kurth and Bein [166], APTES molecules can coat on gold surfaces which have been pre-treated with water molecules. The gold surfaces used in this thesis work have been well treated with water molecules during the cleaning and storage processes. Therefore, APTES molecular networks can also be coated on gold surfaces, assisting the formation of distinct nanoring structures. As shown in Fig 5-9, an array of distinct nanoring structures was formed on gold surface using a template monolayer of 260nm PS nanospheres. In addition, the affinity between PS and hydrophobic gold surfaces will be higher compared with that between PS and hydrophilic silica surface. Hence, enhanced adsorption of PS chains on gold surfaces can be achieved compared with the

adsorption on silica substrate. According to the cross section profile provided in Fig 5-9(C), the ring diameter and height are respectively measured to be 125nm and 13nm, both of which are higher than the measured values for the nanorings generated on silica substrate (Fig 4-5(B)).

Fig 5- 9. (A) 2D, (B) 3D AFM images and (C) cross section profile for nanoring structures generated on gold substrates templated by a monolayer of 260nm PS. The monolayer was stored in air for 2 weeks before applied with a treatment in ethanol solution of 1% APTES for 1hr at room temperature. The scale bar in the insets is 100nm.

Therefore, the versatility of this nanofabrication technique to generate nanoring arrays on alternative substrate surfaces has been demonstrated, provided that the bridging molecules are capable to form molecular networks on the corresponding substrate surface. Meanwhile, it has been demonstrated that, besides the contribution from the interaction between polymer

chains and bridging molecules, the remnant morphologies will also be dependent on the interaction between the polymer chains and the substrate surfaces.

5.4 Metallic Nanoring Structures

The nanoring structures obtained by this nanofabrication technique are constructed by polymer chains with the assistance of bridging molecular networks. This section aims to show the potential to transfer the obtained polymeric nanoring patterns into nanoring structures constructed by other functional materials, despite that the pattern transferring approaches applied here have not been optimized.

For arrays of polymer rings on gold surface, it has been shown that the polymer nanoring patterns are capable to be transferred into the underlying gold layer by applying chemical etching for the gold layer. Before transferring the pattern, it is recommended to pre-treat the obtained polymer nanorings with plasma or UV-Ozone to ensure distinct ring shaped surface coverage on substrate. In a particular pattern transferring approach carried out in this thesis work, polymer nanoring arrays have been generated on gold surfaces by using monolayers of 600nm PS nanospheres as templates. Then, the samples were etched for 10min in an etchant solution composed of KI, I₂ and deionized water in weight ratio of 2:1:1000. Subsequently, the polymer rings were removed by immersing the etched samples in toluene for 10min at 60°C. Fig 5-10(A) is the FESEM image of some of the obtained gold nanorings, showing feasibility, even though the results are far from optimized.

Fig 5- 10. FESEM images of (A) gold nanorings, (B) inverse gold nanorings fabricated by applying the obtained polymer nanoring arrays as templates. The scale bars in the insets are 100nm.

Besides, arrays of inverse ring patterns can also be obtained by the generated polymer nanoring arrays. For example, polymer nanoring arrays have been formed on silica substrates templated by 600nm PS nanosphere monolayers. Subsequently, gold layer with thickness of 15nm was evaporated onto the surface of each sample. In the end, the polymer nanoring arrays were ultrasonically removed by toluene, leaving arrays of inverse gold nanoring structures, as shown in Fig 5-10(B). This indicates the capability of the obtained polymer nanoring arrays to be applied for the formation of inverse ring arrays composed of selective functional materials.

5.5 Chapter Summary

Based on the bridging molecule assisted nanoring fabrication system as introduced in Chapter 4, this chapter has elaborated on the versatility and feasibility of this nanofabrication technique. To summarize, the versatility of this technique has been proved by successful nanoring formation in fabrication systems involving alternative template nanospheres and

alternative substrate surfaces. One critical prerequisite for alternative template nanospheres to achieve nanoring formation is that the nanosphere should be constructed by polymer chains. Template nanospheres composed of non-polymeric materials, like silica, will not be able to contribute to construct the ring shaped remnant nanostructures. On the other hand, for an alternative substrate surface, to ensure the effectiveness of the bridging molecules, the substrate is required to be capable to afford successful surface coating of bridging molecules.

Based on alternative fabrication systems, the effects of template nanospheres and substrate surfaces have also been studied. The influences of template nanospheres on nanoring morphologies are mainly determined by the strength of interaction between the bridging molecules and the relaxed polymer chains along the surface of each template nanosphere. It has been demonstrated that only minor effects on nanoring morphologies can be achieved by the stabilizing surfactant and the charged end groups which were introduced during the synthesis of template nanospheres. Besides, a linear dependence of the nanoring diameter on the square root value of the template nanosphere diameter has been derived. In addition, the nanoring morphologies are also dependent on the interactions between the polymer chains and the substrate surfaces. Higher interacting strength can result in better defined nanoring features.

In the end of this chapter, it has been demonstrated that arrays of gold nanoring and gold inverse ring structures can be generated based on the polymer nanoring arrays obtained by this bridging molecule assisted nanofabrication technique, which demonstrates the feasibility of this technique to produce diverse nanoring structures composed of functional materials.

CHAPTER 6: Manipulating Nanoring Morphologies by Tailored Swelling of Template Nanospheres

According to the studies in Chapter 4 and Chapter 5, it has been concluded that successful generation of nanoring structures relies on the interaction among the bridging molecules, the substrate and the expanded tangling polymers along the template nanosphere surfaces. Hence, the relaxation process of template nanospheres is proposed to be another critical factor for nanoring formation. However, all the previous analyses regarding the influence of each system component were based on a common relaxation history, since all the involved template monolayers have been stored in atmosphere ambient for 2 weeks before usage. Therefore, in this chapter, a study focusing on manipulation of the relaxation processes will be carried out. The relaxation processes have been tailored based on 3 major aspects: relaxation time, surrounding vapor, and ambient temperature.

6.1 Effects of Relaxation Time on Nanoring Formation

Once polymers are brought to interact with a surrounding solvent, the solvent molecules will firstly wet the polymers, and then diffuse into the polymers. For polymeric nanospheres placed in room temperature ambient which is well below the glass transition temperature, the nanospheres will be in a glassy state which leads to a slow diffusion process of the solvent molecules into the polymer matrices. This is known as non-Fickian diffusion which is referred to as case II swelling [169]. In such situation, generally, the solvent molecules will

firstly plasticize the polymers at the interface to reduce the glass transition temperature of these polymers. Consequently, a rapid swelling of the plasticized surface polymers will take place, and the diffused solvent molecules will start to attack the polymers at the freshly exposed boundary. This boundary is defined as the interface between the highly swollen surface region and the unswollen neighboring region. Subsequently, through the thermal molecular motion of the swollen polymers along the template nanosphere surface, as discussed in section 4.2 of Chapter 4, some of these swollen polymers will accumulate around the contact site between the template nanosphere and the substrate.

Fig 6-1 shows the footprint arrays obtained by directly peeling off template PS nanosphere monolayers which have been stored for various durations before usage. For the monolayer which was peeled off after it was dried thoroughly in atmosphere ambient for overnight, little remnants could be observed as shown in Fig 6-1(A) and Fig 6-1(B). For the one which was stored for 1 week in air before peeling off, some remnants could be observed from the AFM images of Fig 6-1(C) and Fig 6-1(D). However, ring shaped footprint morphology is not sufficiently clear and uniform. As provided by Fig 6-1(E) and Fig 6-1(F), distinct ring shaped footprints could not be observed until the monolayer has been stored for 2 weeks in air. This indicates a slow process for the swollen surface polymers to accumulate around the contact site.

Fig 6- 1. AFM images of remnants on silica substrates obtained by direct peeling off PS monolayers which have been stored in atmosphere ambient for (A) & (B) overnight, (C) & (D) 1 week, and (E) & (F) 2 weeks.

Fig 6-2 shows the AFM images of the remnant arrays on silica substrates obtained by template monolayers of PS nanospheres which have been stored for various durations before

usage. All of the monolayers have been treated with standard bridging molecule treatment (ethanol solution of 1% APTES at room temperature for 1hr) before peeling off. It was found that remnants with distinct and complete ring shaped morphologies could not be observed until the monolayer has been stored for 1 week (Fig 6-2(C) and Fig 6-2(D)) in atmosphere ambient before usage, which also indicates a slow process for swelling of surface polymers in air phase.

For the monolayer which was immediately applied with APTES treatment after it was dried thoroughly, as shown in Fig 6-2(A) and Fig 6-2(B), although the ring shaped morphology is not well defined, some remnants can still be obtained on the substrate. This may be caused by some side contributions which only show minor effects in a well relaxed system. Despite the insignificant influence from the treatment solvent on the accumulation of polymer chains (as discussed in section 4.2 of Chapter 4), by changing the surrounding environment from atmosphere ambient to ethanol solvent, the swelling of surface polymers can be enhanced to some extent. Hence, a few expanded surface polymer chains can be anchored onto the substrate by the bridging molecular network. In addition to such swelling effects by the treatment solvent, additional molecular adsorption will also contribute to remnant volume due to attractive electrostatic interactions between the bridging molecules with the ionic stabilizing surfactants or the charged end groups of polymer chains. Nevertheless, all these effects could only provide minor contribution to nanoring formation, which leads to incomplete ring shaped remnant morphologies.

For PS nanospheres located in atmosphere ambient, both the swelling and thermal motion of the surface polymer chains are slow processes. Although reduced interfacial free energy could be achieved by moving the nanospheres from water solvent to air environment, it still

preserves a high value of interfacial free energy between the air phase and the hydrocarbon chains. For instance, the reported interfacial energy of PS/air is around 40.7mJ/m^2 [170], which is much larger compared with the reported value for the PS/ethanol interface (6.2mJ/m^2) [170] or for the PS/toluene interface (less than 2mJ/m^2) [171]. The high interfacial energy indicates weak interaction between the PS nanosphere surface and the air phase, which results in slow swelling and thermal motion of the PS chains at the nanosphere surface.

Fig 6- 2. AFM images of remnants on silica substrates templated by PS monolayers which have been stored in atmosphere ambient for (A) & (B) overnight, and (C) & (D) 1 week before being treated with ethanol solution of 1% APTES at room temperature for 1hr.

6.2 Enhanced Swelling of Template Nanospheres by Solvent Vapor Annealing

As concluded in previous section, the relaxation of surface polymers in an air environment is slow. It requires weeks of storage for the samples to allow sufficient expansion of the surface molecules before applying the bridging molecule treatment to produce arrays of well defined nanoring features. Therefore, it is essential to refine the fabricating system to reduce the processing time. The slow relaxation of the surface polymers is mainly caused by the weak interaction between the polymers and the air phase. Hence, faster relaxation may be obtained by replacing the atmospheric phase with another vapor phase which preserves stronger interaction with the surface polymer chains.

6.2.1 Solubility Parameter Mediated Mixing Behaviors

Upon mixing of polymers with surrounding solvent molecules, the change in Gibbs' free energy of the mixture can be expressed as

$$\Delta G_M = \Delta H_M - T\Delta S_M \quad \text{Eq(6-1)}$$

where T is the absolute temperature, ΔH_M and ΔS_M are, respectively, the enthalpy and entropy of mixing. Generally, a negative ΔG_M leads to spontaneous mixing. The entropy of the system will always be increased due to mixing, which indicates a positive value of $T\Delta S_M$. Negative value of ΔH_M can be induced by mixing two species which can attractively interact with each other, such as acidic component mixing with base component, or two species with opposite polarities. Nevertheless, for most nonpolar organic molecules, a positive heat of mixing will result from the following equation [172]:

$$\Delta H_M = V_M[\delta_1 - \delta_2]^2 v_1 v_2 \quad \text{Eq(6-2)}$$

where V_M is the total volume of the mixing system, and v_i represents the volume fraction of component i in the mixture. δ_i is the solubility parameter of component i which is defined to be equal to the square root value of its cohesive energy density. This relationship only exists for systems with a positive heat of mixing, which is true for the majority of organic polymer mixtures. According to Eq(6-2), it can be deduced that a minimum value for heat of mixing can be obtained by mixing two components with similar solubility parameters. Therefore, the tendency for two components to mix will be higher if their solubility parameters are closer to each other, which is accepted to be a common notion in chemistry known as “like dissolves like”.

The solubility parameters of some species are summarized in Table 6-1 [173, 174]. It is difficult to obtain significant swelling and dissolving effects if the solubility parameter difference between the solvent and polymer is larger than $3.5\text{MPa}^{1/2}$ [175]. According to Table 6-1, both acetone and toluene vapors should be able to swell the PS nanospheres, while toluene vapor provides much more significant swelling effects compared with acetone vapor.

Table 6- 1. List of solubility parameters.

	PS	Water	Ethanol	Acetone	Toluene
Solubility parameter δ ($\text{MPa}^{1/2}$)	17.8 to 18.6 (molecular weight dependent)	47.9	26.5	20.3	18.2

6.2.2 Experiment Set-up for Vapor Annealing

Monolayers of 260nm PS nanospheres on silica substrates were subjected to vapor annealing as soon as they were dried on silica substrates in air ambient. The annealing processes were carried out by the set-up as shown in Fig 6-3. A container was filled with annealing solvent (acetone or toluene) in amount of 1/3 of its total volume. Samples of nanosphere monolayers were placed in the vapor ambient with the help of a physical support. Then the container was sealed and kept undisturbed for certain time duration. After being removed from the solvent vapor environment, the annealed monolayers underwent the standard bridging molecule treatment.

Fig 6- 3. Schematic illustration of the set-up for vapor annealing.

6.2.3 Effects of Acetone Vapor Annealing

Fig 6-4 shows the nanoring arrays generated by monolayers which have been annealed with acetone vapor for various durations. It could be observed that, by increasing the annealing time from 30min (Fig 6-4(A&B)) to 60min (Fig 6-4(C&D)) and 90min (Fig 6-4(E&F)), the obtained ring diameter will be accordingly increased from 90nm to 105nm and 155nm. All of these values are larger than the one generated by the monolayer without vapor annealing (Fig

6-5(A), measured diameter 70nm)

Fig 6- 4. 3D AFM images and cross section profiles for nanoring structures generated by 260nm PS monolayers which have been annealed with acetone vapor for (A, B) 30min, (C, D) 60min, and (E, F) 90min. All these monolayers were annealed immediately after drying in air, and all of the annealed samples were treated with 1% APTES for 1hr at room temperature. The scale bars in the insets are 100nm.

Fig 6- 5. (A) Cross section profile of the remnant structures generated by a monolayer without annealing, which corresponds to the one shown in Fig 6-2(A&B). (B, C) Cross sectional FESEM images of monolayers annealed with acetone vapor for (B) 60min, and (C) 90min. (D) Schematic illustration about the reduction in effective surface area due to flattened contact area.

As discussed above, acetone has a solubility parameter which is close to that of PS, indicating a high tendency for the acetone vapor molecules to swell the polymer chains of PS nanospheres. The increased ring diameter is proposed to result from the form factor change of the template nanosphere due to swelling effects. Annealing with longer duration gives rise

to more significant swelling effects, leading to larger changes in shape of the template nanospheres. This is supported by the FESEM images of Fig 6-5(B) and Fig 6-5(C) which show the cross section views of the 260nm PS monolayers after acetone vapor annealing for 60min and 90min, respectively. It can be found that, after annealing for 60min, the shape of the nanospheres is not ideally spherical. Flattened contact areas between the nanospheres and the substrate can be observed. By further increasing the annealing time to 90min, the swollen PS nanoparticles will merge with each other to form a polymer film, while the shape of individual nanoparticle becomes difficult to categorize.

However, since all the annealed samples underwent bridging molecule treatment in ethanol solution, the swollen entanglement of polymer chains will be compacted upon being moved from acetone vapor to ethanol solvent. This reduces the overall swelling effects of acetone annealing. Besides, the change in volume for each nanoring structure with increasing annealing time should be a compromised result which is dependent on several factors.

Upon increasing annealing time, the swelling of the surface polymer chains can be enhanced. Hence, the expanded polymers and the bridging molecular network introduced in subsequent treatment can interpenetrate with each other more effectively, leading to increasing remnant volume. In addition, as discussed in the beginning of section 6.1, the swelling of polymers at a temperature below glass transition temperature will follow the behavior of non-Fickian diffusion [169], where a moving boundary between swollen and unswollen surface regions will exist during the mixing process. Therefore, after the polymers in the surface region of a nanosphere have been extensively swelled due to vapor annealing, by further increasing the annealing time, the polymer chains in the inner region will start to be swelled. In other words, increasing annealing time can result in increased thickness of the swollen polymer layer,

which leads to more expanded surface polymers contributing to the final remnant volume.

On the other hand, as shown in Fig 6-5(D), since the swollen nanospheres after vapor annealing will preserve a flattened contact area on the substrate, the surface area of the PS sphere which is effective in contributing surface chains for nanoring formation will be reduced due to the curvature change around the contact area. This acts as an opposing factor for the increment in remnant volume with annealing time. Therefore, as shown in Fig 6-4, only a slight increment in the overall volume of each nanoring can be obtained by increasing annealing time. Despite the increasing ring diameter, it was found that the ring heights for the three samples shown in Fig 6-4 are all below 2nm, comparable with the unannealed remnant structures (Fig 6-5(A)).

6.2.3 Effects of Toluene Vapor Annealing

Fig 6-6 shows the nanoring arrays generated by monolayers which have been annealed with toluene vapor for various durations. It could be observed that, compared with those generated by acetone annealing, better defined nanoring features with larger values of ring heights can be obtained by toluene vapor annealing. According to Table 6-1, toluene vapor can swell the PS nanospheres more significantly compared with acetone vapor. Hence, despite the opposing effects from the treatment solvent, the overall swelling of the tangling PS chains will be more significant for the samples annealed with toluene vapor, which leads to accumulation of more polymer chains after treatment of bridging molecules. Meanwhile, similar to the effects of acetone annealing, toluene vapor annealing will also induce shape change of template PS nanospheres, which results in larger ring diameters compared with the one without annealing (Fig 6-5(A)). By increasing the annealing time from 10min (Fig 6-

6(A&B)) to 30min (Fig 6-6(C&D)), the obtained ring diameter will be increased from 80nm to 90nm due to the enhanced shape change.

Fig 6- 6. AFM images and cross section profiles for nanoring structures templated by monolayers of 260nm PS nanospheres which have been annealed with toluene vapor for (A, B) 10min, and (C, D) 30min. All these monolayers were annealed immediately after drying in air, and all of the annealed samples were treated with 1% APTES for 1hr at room temperature. The scale bars in the insets are 100nm.

Nevertheless, the swollen nanospheres will start to merge with neighboring nanoparticles after annealing with toluene vapor for 50min (Fig 6-7(A)), while a completely merged polymer film will be formed when the annealing duration is increased to 60min (Fig 6-7(B)). For the samples annealed with acetone vapor, merged polymer film will not be formed until 90min annealing (Fig 6-5(C)). This shows a faster swelling and merging process for toluene annealed samples compared with those annealed with acetone.

Fig 6- 7. FESEM images of tilted views of monolayers annealed with toluene vapor for (A) 50min and (B) 60min.

At room temperature, compared with acetone, toluene has a lower saturated vapor pressure, implying smaller amount of toluene vapor molecules in the sealed annealing chamber at equilibrium. Meanwhile, toluene also has a lower evaporation rate than acetone, implying a slower process for toluene molecules to be vaporized into the vapor phase. Hence, for the same annealing duration, there will be a lower density of toluene molecules in the annealing vapor compared with the density of acetone vapor molecules. Despite this, more significant swelling of polymer chains takes place. Thus, it can be deduced that the tendency to swell the tangling PS chains is much higher for toluene vapor molecules than that for acetone molecules, which further indicates the critical effects of the solubility parameters on the mixing behavior.

According to the discussions about the vapor annealing processes with toluene and acetone, it is can be inferred that both the ring diameter and height can be tuned through vapor annealing with organic solvents. For annealing system involving small difference in solubility parameters between the annealing solvent and the nanosphere polymer, like toluene

and PS, significant enhancement in ring height can be achieved, which provides higher potential in ring height manipulation. However, such system will give rise to faster swelling and merging of template nanospheres, which reduces the feasibility to tune the ring diameter. On the other hand, for annealing system with increased difference in solubility parameters between the polymer and the annealing solvent, like PS and acetone, the swelling and merging process of template nanospheres will be slower, leading to higher feasibility in manipulation of ring diameter. However, this will sacrifice the swelling tendency, which reduces the enhancement in ring height. Therefore, vapor annealing will result in competing effects on manipulations of ring height and ring diameter. Geometrical tailoring of nanoring structures can be achieved by manipulating the effects of solubility parameters based on material selection for template polymer nanospheres and annealing solvent, together with the adjustment in annealing process (time and temperature).

6.2.4 Potential for Generation of Multi-ring Structure by Vapor Annealing

According to the discussions above, it can be concluded that vapor annealing by organic solvents can accelerate the relaxation of the template nanospheres, which can be further applied to tune the ring geometries. All the template monolayers for the above annealing processes were used immediately after drying. This thesis work has also studied the effects of solvent vapor annealing for template monolayers which have already been well relaxed. As shown in Fig 6-8, a monolayer of 260nm PS nanospheres has been stored in air for 2 weeks before usage. Then, the well relaxed sample was annealed in acetone vapor for 90min and subsequently treated with the standard bridging molecule treatment. The remnant morphologies obtained after peeling off the treated monolayer can be observed from the

AFM images in Fig 6-8(A&B). Double ring morphologies can be seen, although the ring shaped structures are not well defined. The cross section profile for one of the remnant structures is provided in Fig 6-8(C), which also indicates double ring morphology for that nanostructure.

Fig 6- 8. (A) 2D and (B) 3D AFM images and (C) cross section profile for remnant structures templated by a monolayer of 260nm PS nanospheres which has been annealed with acetone vapor for 90min. The monolayer was stored in air for 2 weeks before annealing, and the annealed sample was treated with 1% APTES for 1hr at room temperature. The scale bar in the inset is 100nm.

For each template nanosphere, after storing for 2 weeks in air, some expanded surface polymer chains will be able to accumulate around the contact site due to thermal motion. These polymers chains will construct a ring shaped structure which will remain on the substrate after removing the template nanosphere. This accumulation will have a diameter around 55nm, as measured by Fig 4-5(A) in Chapter 4. In subsequent vapor annealing process, the bottom part of the swollen nanosphere will collapse onto the substrate, covering the ring shaped accumulation, as illustrated in the inserted schematic of Fig 6-8(C). Upon removing the template nanosphere after treatment of bridging molecules, the ring shaped accumulation will induce additional adsorption of some polymer chains covering on it due to hydrophobic interaction, resulting in ring shaped remnant with increased diameter (70nm as shown for the inner ring of Fig 6-8(C)) compared with the original value (55nm). Meanwhile, the remnant contributed from the outer surface of the swollen template nanosphere will be observed as the outer ring. The measured diameter for the outer ring is around 150nm Fig (6-8(C)), which matches very well with the one measured for the sample of 6-4(E&F). Accordingly, it seems possible that multi-ring structures are achievable by tailoring the relaxation of the template nanospheres.

6.3 Accelerated Relaxation of Template Nanospheres by Thermal Annealing

In a system of mixing polymers and surrounding solvent molecules, besides the solubility parameters of the two species, the ambient temperature is another critical factor which determines the mixing dynamics of the system. Temperature acts as a scaling factor for the effect of the entropy of the system, represented by the term $T\Delta S_M$ in Eq (6-1). Higher

temperature will result in larger value of the entropy term and thus lower Gibbs free energy of the system, leading to higher tendency for the two species to mix. Therefore, besides solvent vapor annealing, it is reasonable to expect that thermal annealing of the template monolayers can be another effective way to accelerate the relaxation of the surface polymer chains as well as to manipulate the nanoring morphologies.

Fig 6-9 shows the nanoring arrays generated by monolayers of 260nm PS nanospheres which have been annealed at 60°C on a hotplate for various durations. All the monolayer samples were annealed immediately after drying in air. After thermal annealing, the annealed monolayers went through the standard process of bridging molecule treatment. Nanostructures with more complete and distinct ring shaped morphologies can be obtained compared with the one without thermal annealing (Fig 6-5(A)), which indicates the accelerating relaxation of surface polymers by thermal annealing.

In addition, by increasing the thermal annealing time from 1hr (Fig 6-9(A&B)) to 4hr (Fig 6-9(C&D)) and 8hr (Fig 6-9(E&F)), the obtained ring diameter will be accordingly increased from 80nm to 100nm and 110nm. All of these values are larger than the measured value for the one without annealing which is around 70nm as shown in Fig 6-5(A). Similar as vapor annealing, since thermal annealing can enhance the swelling of polymer chains along the nanosphere surface, shape change of the template nanosphere will result upon the thermal annealing. Longer annealing duration gives rise to larger changes in shape of the nanospheres, leading to increased diameters of the ring shaped remnants after removing template nanospheres. This indicates the feasibility of thermal annealing to manipulate the nanoring dimensions.

Fig 6- 9. 3D AFM images and cross section profiles for nanoring structures generated by 260nm PS monolayers which have been annealed at 60°C on a hotplate for (A, B) 1hr, (C, D) 4hr, and (E, F) 8hr. All these monolayers were annealed immediately after drying in air, and all of the annealed samples were treated with 1% APTES for 1hr at room temperature. The scale bars in the insets are 100nm.

The change in ring volume with increasing thermal annealing durations should be dependent on the compromised results between increased polymer accumulations due to enhanced swelling and reduced effective surface area due to flattened contact area. For annealing duration from 0hr (no annealing) to 1hr and further to 4hr, the swelling of the polymer chains can be well enhanced upon increasing annealing time, which leads to increased remnant

volume despite the reduced effective surface area.

The glass transition temperature of bulk PS is around 100°C [176]. The polymers located in the surface region will have a glass transition temperature which is lower than the one for bulk material [157, 158]. Hence, by annealing the polymers at 60°C which is not far below the glass transition temperature, the swelling behaviors of the polymers will be different from the non-Fickian diffusion [169] as described for interaction at room temperature. The moving interface between swollen and unswollen region will become less distinguishable. Therefore, after the polymers of a nanosphere have been extensively swelled due to thermal annealing, only minor influences can be achieved by further increasing the annealing time to increase the thickness of the swollen polymer layer. Hence, the enhancement in polymer accumulation due to such additional annealing duration would be insignificant. Meanwhile, due to increasing flattened contact area, the effective surface area is decreased. This explains the reducing ring volume upon increasing the annealing time from 4hr (Fig 6-9(C&D)) to 8hr (Fig 6-9(E&F)).

6.4 Chapter Summary

To summarize, in atmospheric environment, both the relaxation of polymers along the template nanosphere surface and the thermal motion of these relaxed surface polymer chains are slow processes. The template monolayers need to be stored in air for weeks to ensure the formation of distinguishable ring shaped nanostructures, leading to long processing duration which is undesirable. The slow process is proposed to be mainly caused by the weak interaction of polymer molecules with the surrounding air environment at room temperature.

By replacing the air environment with organic solvent vapor (vapor annealing) or by increasing the relaxation temperature (thermal annealing), it can be shown that acceleration in the relaxation of polymer chains can be achieved, effectively reducing the total processing time from weeks to hours. In addition, both vapor annealing and thermal annealing have shown the feasibilities to manipulate the remnant diameters and volumes. Besides, based on vapor annealing, it has also been demonstrated that it is feasible to fabricate multi-ring structures by tailoring the relaxation of the template nanospheres.

CHAPTER 7: Conclusions and Future Work

7.1 Conclusions

This thesis has established a nanoscale patterning technique to produce long range periodic arrays of nanorings by applying 2D polymeric nanosphere colloidal crystals as the templates. The simple process control and versatility of this technique have been illustrated. The tunability in nanoring geometries and array constants has also been demonstrated by tailoring the swelling of the template polymeric nanospheres. The following summarizes the major contributions of the research work:

1. Exploring a novel perspective of colloidal lithography

In almost all of the existing colloidal lithography techniques, the template colloidal nanoparticles are treated as assembled entities to define the positions and geometries of the target nanostructures. As an extension to such conventional roles, this work has explored a novel perspective to make use of the colloidal nanoparticles as the reservoirs of patterning materials. For polymeric colloidal nanoparticles constructed by thermoplastic chains, each colloid is a cluster of entangled individual polymer chains. Hence, in the perspective of this work, each colloidal nanoparticle is treated as an ensemble of polymer chains, where the elementary building blocks are the individual molecular chains. Through particular manipulations, individual polymer molecules can be acquired from the bulk ensemble to construct target nanostructures, preserving the positions and geometries defined by the bulk ensemble. Based on the establishment of such perspective, novel routes of colloidal lithography can be inspired and developed.

2. Demonstrating molecular dynamics of the polymer chains located in the surface region of a polymeric colloidal nanoparticle.

Based on the observation of ring shaped footprint arrays generated by directly peeling off the monolayers of polymer nanospheres from the substrates, it has been deduced that the surfaces of polymeric nanoparticles are not stable. By reducing the interfacial free energy between the environment and the nanoparticles, the polymer chains at the surface of each nanoparticle will relax to more loosely packed entanglement. In the region close to the substrate surface, some polymer chains can reach the substrate surface through molecular thermal motions during the relaxation process.

It has been demonstrated that the relaxation of polymers at nanoparticle surface is a slow process in atmosphere ambient due to the weak interaction between polymer molecules and the air environment at room temperature. Acceleration in relaxation of polymer chains can be achieved by increasing the relaxation temperature (thermal annealing) or by replacing the air environment with organic solvent vapor (vapor annealing) which can effectively swell the polymers.

3. Establishing a versatile approach to generate nanoring arrays

A nanosphere lithography approach assisted by bridging molecule treatment has been established to generate arrays of well defined polymeric nanoring features. The formation of nanoring structures is mainly realized by the interpenetration and attractive interactions between the bridging molecular networks and the loosely entangled polymer chains at the surface of the template nanospheres. Importantly, arrays of gold nanorings and gold inverse rings have been generated based on the obtained polymeric nanoring arrays, which shows the

capability of this technique to produce diverse forms of functional nanoring arrays.

The versatility and feasibility of this technique have been demonstrated by successful formation of nanoring arrays in alternative fabrication systems involving different bridging molecules, template nanospheres and substrate surfaces. Based on this, a systematic study about the formation mechanisms of nanoring structures has been carried out, and the prerequisites for each element of a potential fabrication system have been established.

4. Circumventing the limitations of existing techniques

For the fabrication technique of nanoring arrays reported by this thesis work, the only external additive involved in the fabrication system is the bridging molecules. The interaction of the bridging molecules with other elements of the fabrication system does not require any specific control, which ensures an easy process control for this method. Besides, a linear dependence of the nanoring diameter on the square root of the template nanosphere diameter has been derived and verified, which indicates the capability of this technique to tune the nanoring dimensions by incorporating relative lattice constants. In addition, through tailoring the form factor of the template nanospheres by thermal annealing or vapor annealing, it shows the ability of the technique to manipulate the nanoring geometries at fixed particular lattice constants. Moreover, the feasibility to fabricate multi-ring arrays has also been demonstrated by manipulating the vapor annealing processes of the template nanospheres. To conclude, the fabrication approach established in this work preserves both easy process control and tunability of nanoring geometries, which circumvents the key limitations of existing nanofabrication techniques for nanoring arrays.

7.2 Recommendations for Future Work

7.2.1 Improving Efficiency of Surface Molecular Transfer

A straightforward opportunity for future activities is to improve the final nanoring features based on the perspective of colloidal lithography established in this work. Here, the patterning polymer molecules are captured from the template nanosphere reservoir by bridging molecular networks. The future work can be based on exploring bridging molecules with improved bridging effects, which can effectively enhance the localized adsorption of polymer chains. Alternatively, the approaches to capture patterning molecules can be designed to avoid the involvement of bridging molecules but incorporate some other bridging processes which are more effective to capture the surface polymer chains, giving rise to more distinct nanoring features.

7.2.2 Controlling Orientation of Nanoring Array

In this thesis, the demonstrated ethanol spreading method for the fabrication of template colloidal crystals is limited in controlling the alignment directions of the template nanospheres, which further restricts the registration capability of the nanoring arrays. However, some applications of nanoring arrays in surface enhanced spectroscopies will be sensitively affected by the incident angle relative to the nanoring array's crystallographic axes. Hence, it will be a good opportunity for future works to incorporate registration of alignment direction into the nanoring arrays by controlling the in-plane orientations of the template colloidal monolayers. For instance, a meniscus pinning method can be applied to achieve unidirectional growth of colloidal monolayers, in which a linear meniscus line can be well controlled by optimizing the withdrawal speed and pinning boundary [177]. Based on

such alignment technique, it becomes feasible to achieve multilayer structures of aligned nanoring arrays through the establishment of well-designed layer by layer fabrication approaches.

7.2.3 Diversifying Morphology of Nanoring Array

In addition, the ethanol spreading method can only generate close packed template monolayers in hexagonal symmetry. This restricts the pattern diversity of the resulted nanoring arrays. Therefore, another opportunity for future activities is to create diverse symmetries and patterns for the final nanoring arrays. One recommended way to establish such diversity is to deposit close packed monolayers on soft substrates, such as Polydimethylsiloxane (PDMS) mold. Through this way, the patterns of the template monolayers can be tuned by isotropic expansion or anisotropic stretching of the soft mold. Subsequently, the manipulated soft mold can be transferred onto desirable substrates, either flat or curved, giving rise to even larger tunability in the final forms of nanoring arrays [144]. Moreover, arrays of elliptical nanorings can also be generated by further uniaxial stretching of the soft mold after circular nanorings are formed on the soft mold [110]. Another way to improve the diversity is to fabricate template colloidal crystals with other symmetries besides hexagonal arrangement. For instance, binary colloidal superlattices can be obtained by a binary mixture of oppositely charged polymeric nanospheres [178]. Various superlattice structures can be prepared by manipulating the charge magnitudes or the dimensions of the template colloids. For the fabrication method of ordered nanoring arrays developed by this thesis, 3D colloidal crystals can also be applied as the templates. In such cases, the pattern of the bottom layer which contacts the substrate surface will be transferred into the pattern of the resulted nanoring arrays. Therefore, by exploring the symmetry diversity of the template

colloidal crystals, a rich variety of nanoring patterns can be realized.

7.2.4 Exploring Production and Application of Functional Nanoring Arrays

Another opportunity for future work is to explore the production and application of diverse forms of functional nanoring arrays based on the obtained polymeric nanoring arrays. Up to date, some conventional pattern-transfer techniques such as chemical etching [66], ion milling [144], and physical deposition [32] have already been well established. On the other hand, unconventional approaches like electroless plating [139] or chemical implantation [138] are also good choices to transfer the patterns of the polymeric nanoring arrays into functional nanorings constructed by other materials.

A large number of applications can be developed depending on the materials of the nanorings. Especially for nanoring arrays constructed by noble metals, they are regarded as promising candidates for the applications of NIR nanoplasmonic sensing due to the tunability of LSPR in the NIR spectral range, the uniformly distributed field enhancement at resonant condition, as well as the large exposed empty volume of each nanoring cavity. Fig 7-1 shows a prototype to apply the fabricated functional nanoring array as a sensing device. The nanoring array is integrated with a transparent flow cell by sealing the nanoring array (on glass substrate) with another cover glass. Instead of glass, other transparent materials which show minimum optical absorption in the NIR range can also be applied as the solid supports on both sides. A layer of silicone isolator with predefined fluidic channel is applied to seal the glass substrate with the cover glass. Inlet and outlet holes are mechanically drilled on the cover glass. Injection tubes can be inserted through the holes into the fluidic channel, and sealed with the holes by bonding PDMS blocks to the cover glass. Upon introducing target

solution into the sensing device, the transmission of linearly polarized NIR light beam is recorded, based on which the extinction spectrum can be further calculated.

Fig 7- 1. Prototype to apply the fabricated functional nanoring array as a sensing device.

REFERENCES

1. Halas, N.J., et al., *Plasmons in Strongly Coupled Metallic Nanostructures*. Chemical Reviews, 2011. **111**(6): p. 3913-3961.
2. Cortie, M.B. and A.M. McDonagh, *Synthesis and Optical Properties of Hybrid and Alloy Plasmonic Nanoparticles*. Chemical Reviews, 2011. **111**(6): p. 3713-3735.
3. Hartland, G.V., *Optical Studies of Dynamics in Noble Metal Nanostructures*. Chemical Reviews, 2011. **111**(6): p. 3858-3887.
4. Mayer, K.M. and J.H. Hafner, *Localized Surface Plasmon Resonance Sensors*. Chemical Reviews, 2011. **111**(6): p. 3828-3857.
5. Lal, S., et al., *Tailoring plasmonic substrates for surface enhanced spectroscopies*. Chemical Society Reviews, 2008. **37**(5): p. 898-911.
6. Okamoto, T., I. Yamaguchi, and T. Kobayashi, *Local plasmon sensor with gold colloid monolayers deposited upon glass substrates*. Opt. Lett., 2000. **25**(6): p. 372-374.
7. Jensen, T.R., G.C. Schatz, and R.P. Van Duyne, *Nanosphere Lithography: Surface Plasmon Resonance Spectrum of a Periodic Array of Silver Nanoparticles by Ultraviolet-Visible Extinction Spectroscopy and Electrodynamical Modeling*. The Journal of Physical Chemistry B, 1999. **103**(13): p. 2394-2401.
8. Hanarp, P., M. Käll, and D.S. Sutherland, *Optical Properties of Short Range Ordered Arrays of Nanometer Gold Disks Prepared by Colloidal Lithography*. The Journal of Physical Chemistry B, 2003. **107**(24): p. 5768-5772.
9. Shumaker-Parry, J.S., H. Rochholz, and M. Kreiter, *Fabrication of Crescent-Shaped Optical Antennas*. Advanced Materials, 2005. **17**(17): p. 2131-2134.
10. Nehl, C.L., H. Liao, and J.H. Hafner, *Optical Properties of Star-Shaped Gold Nanoparticles*. Nano Letters, 2006. **6**(4): p. 683-688.
11. Averitt, R.D., D. Sarkar, and N.J. Halas, *Plasmon Resonance Shifts of Au-Coated Au₂S Nanoshells: Insight into Multicomponent Nanoparticle Growth*. Physical Review Letters, 1997. **78**(22): p. 4217-4220.
12. Link, S., M.B. Mohamed, and M.A. El-Sayed, *Simulation of the Optical Absorption Spectra of Gold Nanorods as a Function of Their Aspect Ratio and the Effect of the Medium Dielectric Constant*. The Journal of Physical Chemistry B, 1999. **103**(16): p. 3073-3077.
13. Aizpurua, J., et al., *Optical Properties of Gold Nanorings*. Physical Review Letters, 2003. **90**(5): p. 057401.
14. Ringler, M., et al., *Moving Nanoparticles with Raman Scattering*. Nano Letters, 2007. **7**(9): p. 2753-2757.
15. Nordlander, P. and E. Prodan, *Plasmon Hybridization in Nanoparticles near Metallic*

- Surfaces*. Nano Letters, 2004. **4**(11): p. 2209-2213.
16. Liu, H., et al., *Magnetic plasmon hybridization and optical activity at optical frequencies in metallic nanostructures*. Physical Review B, 2007. **76**(7): p. 073101.
 17. Maier, S.A. and H.A. Atwater, *Plasmonics: Localization and guiding of electromagnetic energy in metal/dielectric structures*. Journal of Applied Physics, 2005. **98**(1): p. 011101-10.
 18. Bozhevolnyi, S.I., et al., *Channel plasmon subwavelength waveguide components including interferometers and ring resonators*. Nature, 2006. **440**(7083): p. 508-511.
 19. Lal, S., S. Link, and N.J. Halas, *Nano-optics from sensing to waveguiding*. Nat Photon, 2007. **1**(11): p. 641-648.
 20. Zhang, J., et al., *Single-Molecule Studies on Fluorescently Labeled Silver Particles: Effects of Particle Size*. The Journal of Physical Chemistry C, 2007. **112**(1): p. 18-26.
 21. Tseng, H.-Y., et al., *Au nanorings for enhancing absorption and backscattering monitored with optical coherence tomography*. Nanotechnology, 2010. **21**(29): p. 295102.
 22. Lee, C.K., et al., *Characterizing the localized surface plasmon resonance behaviors of Au nanorings and tracking their diffusion in bio-tissue with optical coherence tomography*. Biomedical Optics Express, 2010. **1**(4): p. 1060-1074.
 23. Kim, S., et al., *Patterned Arrays of Au Rings for Localized Surface Plasmon Resonance*. Langmuir, 2006. **22**(17): p. 7109-7112.
 24. Larsson, E.M., et al., *Sensing characteristics of NIR localized surface plasmon resonances in gold nanorings for application as ultrasensitive biosensors*. Nano Letters, 2007. **7**(5): p. 1256-1263.
 25. Hao, J. and J. Sabarinathan. *Near infrared surface plasmon resonance of gold nanoring based plasmonic crystals for sensor applications*. in *Nanotechnology, 2009. IEEE-NANO 2009. 9th IEEE Conference on*. 2009.
 26. Tsai, C.-Y., et al., *Plasmonic Coupling in Gold Nanoring Dimers: Observation of Coupled Bonding Mode*. Nano Letters, 2012. **12**(3): p. 1648-1654.
 27. Teo, S.L., et al., *Gold nanoring trimers: a versatile structure for infrared sensing*. Opt. Express, 2010. **18**(21): p. 22271-22282.
 28. Hulteen, J.C., et al., *Nanosphere Lithography: Size-Tunable Silver Nanoparticle and Surface Cluster Arrays*. The Journal of Physical Chemistry B, 1999. **103**(19): p. 3854-3863.
 29. áEl Hallag, I.S. and P. Groot, *Electrochemical deposition of macroporous magnetic networks using colloidal templates*. Journal of Materials Chemistry, 2003. **13**(10): p. 2596-2602.
 30. Moon, J.H., et al., *Colloidal lithography with crosslinkable particles: fabrication of hierarchical nanopore arrays*. CHEMICAL COMMUNICATIONS-ROYAL SOCIETY OF CHEMISTRY, 2005. **32**: p. 4107.
 31. Chen, X., et al., *Colloidal-Crystal-Assisted Imprint for Mesoscopic Structured Arrays and Hierarchical Patterns*. Advanced Materials, 2004. **16**(18): p. 1632-1636.

32. Halpern, A.R. and R.M. Corn, *Lithographically Patterned Electrodeposition of Gold, Silver, and Nickel Nanoring Arrays with Widely Tunable Near-Infrared Plasmonic Resonances*. ACS Nano, 2013.
33. Ito, T. and S. Okazaki, *Pushing the limits of lithography*. Nature, 2000. **406**(6799): p. 1027-1031.
34. Duan, H., et al., *Nanoplasmonics: Classical down to the Nanometer Scale*. Nano Letters, 2012. **12**(3): p. 1683-1689.
35. Frey, L., C. Lehrer, and H. Ryssel, *Nanoscale effects in focused ion beam processing*. Applied Physics A, 2003. **76**(7): p. 1017-1023.
36. Xia, Y. and G.M. Whitesides, *SOFT LITHOGRAPHY*. Annual Review of Materials Science, 1998. **28**(1): p. 153-184.
37. Hao, F., et al., *Shedding light on dark plasmons in gold nanorings*. Chemical Physics Letters, 2008. **458**(4-6): p. 262-266.
38. Prodan, E., et al., *A Hybridization Model for the Plasmon Response of Complex Nanostructures*. Science, 2003. **302**(5644): p. 419-422.
39. Dutta, C.M., et al., *Plasmonic properties of a metallic torus*. The Journal of Chemical Physics, 2008. **129**(8): p. 084706-9.
40. Ye, J., et al., *Observation of plasmonic dipolar anti-bonding mode in silver nanoring structures*. Nanotechnology, 2009. **20**(46).
41. Liu, S.D., Z.S. Zhang, and Q.Q. Wang, *High sensitivity and large field enhancement of symmetry broken Au nanorings: effect of multipolar plasmon resonance and propagation*. Opt. Express, 2009. **17**(4): p. 2906-2917.
42. Fida, F., et al. *Biosensing Based on Surface Plasmon Resonance of Gold Nanohole and Nanoring Arrays Fabricated by a Novel Nanosphere Lithography Technique*. in *Biocomputation, Bioinformatics, and Biomedical Technologies, 2008. BIOTECHNO '08. International Conference on*. 2008.
43. Gu, Y., Q. Li, and G.P. Wang, *Dielectric supported ring-shaped metal disks on a metal film for ultrasensitive refractive index sensing*. Opt. Lett., 2011. **36**(17): p. 3326-3328.
44. Felidj, N., et al., *Grating-induced plasmon mode in gold nanoparticle arrays*. The Journal of Chemical Physics, 2005. **123**(22): p. 221103-5.
45. Augu, B. and W.L. Barnes, *Collective Resonances in Gold Nanoparticle Arrays*. Physical Review Letters, 2008. **101**(14): p. 143902.
46. Carron, K.T., et al., *Resonances of two-dimensional particle gratings in surface-enhanced Raman scattering*. J. Opt. Soc. Am. B, 1986. **3**(3): p. 430-440.
47. Meier, M., A. Wokaun, and P.F. Liao, *Enhanced fields on rough surfaces: dipolar interactions among particles of sizes exceeding the Rayleigh limit*. J. Opt. Soc. Am. B, 1985. **2**(6): p. 931-949.
48. Lamprecht, B., et al., *Metal Nanoparticle Gratings: Influence of Dipolar Particle Interaction on the Plasmon Resonance*. Physical Review Letters, 2000. **84**(20): p. 4721-4724.

49. Choi, D.-G., et al., *Colloidal Lithographic Nanopatterning via Reactive Ion Etching*. Journal of the American Chemical Society, 2004. **126**(22): p. 7019-7025.
50. Lu, Y., et al., *Nanophotonic Crescent Moon Structures with Sharp Edge for Ultrasensitive Biomolecular Detection by Local Electromagnetic Field Enhancement Effect*. Nano Letters, 2004. **5**(1): p. 119-124.
51. Haynes, C.L., et al., *Angle-Resolved Nanosphere Lithography: Manipulation of Nanoparticle Size, Shape, and Interparticle Spacing*. The Journal of Physical Chemistry B, 2002. **106**(8): p. 1898-1902.
52. Vossen, D.L.J., et al., *Combined Optical Tweezers/Ion Beam Technique to Tune Colloidal Masks for Nanolithography*. Nano Letters, 2005. **5**(6): p. 1175-1179.
53. Near, R., et al., *Pronounced Effects of Anisotropy on Plasmonic Properties of Nanorings Fabricated by Electron Beam Lithography*. Nano Letters, 2012. **12**(4): p. 2158-2164.
54. Kosiorek, A., et al., *Fabrication of Nanoscale Rings, Dots, and Rods by Combining Shadow Nanosphere Lithography and Annealed Polystyrene Nanosphere Masks*. Small, 2005. **1**(4): p. 439-444.
55. Haginoya, C., M. Ishibashi, and K. Koike, *Nanostructure array fabrication with a size-controllable natural lithography*. Applied Physics Letters, 1997. **71**(20): p. 2934-2936.
56. Ozbay, E., *Plasmonics: Merging Photonics and Electronics at Nanoscale Dimensions*. Science, 2006. **311**(5758): p. 189-193.
57. Kretschmann, E. and H. Raether, *Radiative decay of non radiative surface plasmons excited by light(Surface plasma waves excitation by light and decay into photons applied to nonradiative modes)*. Zeitschrift Fuer Naturforschung, Teil A, 1968. **23**: p. 2135.
58. Otto, A., *Excitation of nonradiative surface plasma waves in silver by the method of frustrated total reflection*. Zeitschrift für Physik, 1968. **216**(4): p. 398-410.
59. Kazandjian, L., *Rayleigh methods applied to electromagnetic scattering from gratings in general homogeneous media*. Physical Review E, 1996. **54**(6): p. 6802-6815.
60. Agranovich, V.M. and D.L. Mills, *Surface polaritons: electromagnetic waves at surfaces and interfaces*. 1982: North-Holland Publishing Company.
61. Salomon, L., et al., *Local excitation of surface plasmon polaritons at discontinuities of a metal film: Theoretical analysis and optical near-field measurements*. Physical Review B, 2002. **65**(12): p. 125409.
62. Chen, J., et al., *Evaporation-Induced Assembly of Quantum Dots into Nanorings*. ACS Nano, 2008. **3**(1): p. 173-180.
63. Zheng, Y.B., et al., *Fabrication of tunable nanostructure arrays using ion-polishing-assisted nanosphere lithography*. Journal of Applied Physics, 2006. **99**(3).
64. Bayati, M., et al., *An Approach to Fabrication of Metal Nanoring Arrays*. Langmuir, 2010. **26**(5): p. 3549-3554.
65. Motavas, S., B. Omrane, and C. Papadopoulos, *Large-Area Patterning of Carbon*

- Nanotube Ring Arrays*. Langmuir, 2009. **25**(8): p. 4655-4658.
66. McLellan, J.M., M. Geissler, and Y.N. Xia, *Edge spreading lithography and its application to the fabrication of mesoscopic gold and silver rings*. Journal of the American Chemical Society, 2004. **126**(35): p. 10830-10831.
 67. Sun, Z., et al., *A Universal Approach to Fabricate Various Nanoring Arrays Based on a Colloidal-Crystal-Assisted-Lithography Strategy*. Advanced Functional Materials, 2008. **18**(24): p. 4036-4042.
 68. Zheng, C., in *Micro-Nanofabrication*. 2005, Springer-Verlag Beijing. p. 77-78.
 69. Jaeger, R.C., *Introduction to Microelectronic Fabrication*. 2002, United States of America: Prentice Hall. p. 24.
 70. Wallraff, G.M. and W.D. Hinsberg, *Lithographic imaging techniques for the formation of nanoscopic features*. Chemical Reviews, 1999. **99**(7): p. 1801-1821.
 71. Wisitsoraat, A., et al., *Low-cost and high-resolution x-ray lithography utilizing a lift-off sputtered lead film mask on a Mylar substrate*. Journal of Micromechanics and Microengineering, 2010. **20**(7).
 72. Xie, Q., et al., *Fabrication of nanostructures with laser interference lithography*. Journal of Alloys and Compounds, 2008. **449**(1-2): p. 261-264.
 73. O'Reilly, T.B. and H.I. Smith, *Photoresist characterization using double exposures with interference lithography*. Journal of Vacuum Science & Technology B, 2008. **26**(1): p. 128-131.
 74. Jiang, H.J., et al., *Single-step fabrication of diffraction gratings on hybrid sol-gel glass using holographic interference lithography*. Optics Communications, 2000. **185**(1-3): p. 19-24.
 75. Pepin, A., et al., *Exploring the high sensitivity of SU-8 resist for high resolution electron beam patterning*. Microelectronic Engineering, 2004. **73-4**: p. 233-237.
 76. Girard, C. and E. Dujardin, *Near-field optical properties of top-down and bottom-up nanostructures*. Journal of Optics a-Pure and Applied Optics, 2006. **8**(4): p. S73-S86.
 77. Rahmani, M., et al., *Generation of pronounced Fano resonances and tuning of subwavelength spatial light distribution in plasmonic pentamers*. Optics Express, 2011. **19**(6): p. 4949-4956.
 78. Ebbesen, T.W., et al., *Extraordinary optical transmission through sub-wavelength hole arrays*. Nature, 1998. **391**(6668): p. 667-669.
 79. Grupp, D.E., et al., *Beyond the Bethe Limit: Tunable Enhanced Light Transmission Through a Single Sub-Wavelength Aperture*. Advanced Materials, 1999. **11**(10): p. 860-862.
 80. Menon, R., et al., *Maskless lithography*. Materials Today, 2005. **8**(2): p. 26-33.
 81. Pease, R.F., *Maskless lithography*. Microelectronic Engineering, 2005. **78-79**(0): p. 381-392.
 82. Yao, N., *Focused Ion beam Systems: Basics and Applications*. 2007, Cambridge University Press: Cambridge. p. 2-3.

83. Henzie, J., M.H. Lee, and T.W. Odom, *Multiscale patterning of plasmonic metamaterials*. Nat Nano, 2007. **2**(9): p. 549-554.
84. Hasan, W., et al., *Selective Functionalization and Spectral Identification of Gold Nanopyramids*. The Journal of Physical Chemistry C, 2007. **111**(46): p. 17176-17179.
85. Henzie, J., et al., *Nanofabrication of Plasmonic Structures**. Annual Review of Physical Chemistry, 2009. **60**(1): p. 147-165.
86. Fredriksson, H., et al., *Hole–Mask Colloidal Lithography*. Advanced Materials, 2007. **19**(23): p. 4297-4302.
87. Chen, S., et al., *Ultrahigh sensitivity made simple: nanoplasmonic label-free biosensing with an extremely low limit-of-detection for bacterial and cancer diagnostics*. Nanotechnology, 2009. **20**(43).
88. Fischer, U.C. and H.P. Zingsheim, *Submicroscopic pattern replication with visible light*. Journal of Vacuum Science and Technology, 1981. **19**(4): p. 881-885.
89. Deckman, H.W. and J.H. Dunsmuir, *Natural lithography*. Applied Physics Letters, 1982. **41**(4): p. 377-379.
90. Kralchevsky, P.A. and N.D. Denkov, *Capillary forces and structuring in layers of colloid particles*. Current Opinion in Colloid & Interface Science, 2001. **6**(4): p. 383-401.
91. Denkov, N., et al., *Mechanism of formation of two-dimensional crystals from latex particles on substrates*. Langmuir, 1992. **8**(12): p. 3183-3190.
92. Yan, Q., et al., *Particle and Substrate Charge Effects on Colloidal Self-Assembly in a Sessile Drop*. Langmuir, 2008. **24**(20): p. 11518-11522.
93. ZHAO, Q., et al., *REAL TIME VISUALIZATION OF SURFACTANT EFFECTS ON COLLOIDAL SELF-ASSEMBLY*. International Journal of Nanoscience, 2010. **09**(03): p. 113-118.
94. Rossi, R.C., M.X. Tan, and N.S. Lewis, *Size-dependent electrical behavior of spatially inhomogeneous barrier height regions on silicon*. Applied Physics Letters, 2000. **77**(17): p. 2698-2700.
95. Jiang, P., et al., *Single-Crystal Colloidal Multilayers of Controlled Thickness*. Chemistry of Materials, 1999. **11**(8): p. 2132-2140.
96. Shimmin, R.G., A.J. DiMauro, and P.V. Braun, *Slow Vertical Deposition of Colloidal Crystals: A Langmuir–Blodgett Process?* Langmuir, 2006. **22**(15): p. 6507-6513.
97. Tan, K.W., et al., *Layer-by-Layer Growth of Attractive Binary Colloidal Particles*. Langmuir, 2008. **24**(17): p. 9273-9278.
98. Deckman, H.W. and J.H. Dunsmuir, *APPLICATIONS OF SURFACE TEXTURES PRODUCED WITH NATURAL LITHOGRAPHY*. Journal of Vacuum Science & Technology B, 1983. **1**(4): p. 1109-1112.
99. Hulteen, J.C. and R.P. Van Duyne, *Nanosphere lithography: A materials general fabrication process for periodic particle array surfaces*. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 1995. **13**(3): p. 1553-1558.

100. Lu, Y., Y. Yin, and Y. Xia, *A Self-Assembly Approach to the Fabrication of Patterned, Two-Dimensional Arrays of Microlenses of Organic Polymers*. Advanced Materials, 2001. **13**(1): p. 34-37.
101. Wang, D. and H. Möhwald, *Rapid Fabrication of Binary Colloidal Crystals by Stepwise Spin-Coating*. Advanced Materials, 2004. **16**(3): p. 244-247.
102. Chen, J., et al., *Controllable fabrication of 2D colloidal-crystal films with polystyrene nanospheres of various diameters by spin-coating*. Applied Surface Science, 2013. **270**(0): p. 6-15.
103. Jiang, P. and M.J. McFarland, *Large-Scale Fabrication of Wafer-Size Colloidal Crystals, Macroporous Polymers and Nanocomposites by Spin-Coating*. Journal of the American Chemical Society, 2004. **126**(42): p. 13778-13786.
104. Marczewski, D. and W.A. Goedel, *The Preparation of Submicrometer-Sized Rings by Embedding and Selective Etching of Spherical Silica Particles*. Nano Letters, 2005. **5**(2): p. 295-299.
105. Goldenberg, L.M., et al., *Simple Method for the Preparation of Colloidal Particle Monolayers at the Water/Alkane Interface*. Langmuir, 2002. **18**(14): p. 5627-5629.
106. WangWang, C.J. Summers, and Z.L. Wang, *Large-Scale Hexagonal-Patterned Growth of Aligned ZnO Nanorods for Nano-optoelectronics and Nanosensor Arrays*. Nano Letters, 2004. **4**(3): p. 423-426.
107. Li, Y., et al., *Physical processes-aided periodic micro/nanostructured arrays by colloidal template technique: fabrication and applications*. Chemical Society Reviews, 2013. **42**(8): p. 3614-3627.
108. Yang, S.-M., et al., *Nanomachining by Colloidal Lithography*. Small, 2006. **2**(4): p. 458-475.
109. Moon, J.H., et al., *Multiscale Nanopatterns Templated from Two-Dimensional Assemblies of Photoresist Particles*. Advanced Materials, 2005. **17**(21): p. 2559-2562.
110. Cai, Y., et al., *Fabrication of Elliptical Nanorings with Highly Tunable and Multiple Plasmonic Resonances*. Nano Letters, 2012. **12**(9): p. 4881-4888.
111. Ye, J., et al., *Tuning plasmonic interaction between gold nanorings and a gold film for surface enhanced Raman scattering*. Applied Physics Letters, 2010. **97**(16): p. 163106-3.
112. Ye, J., et al., *Excitation wavelength dependent surface enhanced Raman scattering of 4-aminothiophenol on gold nanorings*. Nanoscale, 2012. **4**(5): p. 1606-1611.
113. Liu, Y.J., et al., *Light-Driven Plasmonic Color Filters by Overlaying Photoresponsive Liquid Crystals on Gold Annular Aperture Arrays*. Advanced Materials, 2012. **24**(23): p. OP131-OP135.
114. Navab, S., S. Goolaup, and A.O. Adeyeye, *Fabrication of large area nanomagnets*. Nanotechnology, 2004. **15**(11): p. 1539.
115. Singh, D.K., et al., *Arrays of ultrasmall metal rings*. Nanotechnology, 2008. **19**(24).
116. Fujii, S., et al., *Fabrication and Placement of a Ring Structure of Nanoparticles by a Laser-Induced Micronanobubble on a Gold Surface*. Langmuir, 2011. **27**(14): p.

- 8605-8610.
117. Hobbs, K.L., et al., *Fabrication of Nanoring Arrays by Sputter Redeposition Using Porous Alumina Templates*. Nano Letters, 2003. **4**(1): p. 167-171.
 118. Cho, H., et al., *Fabrication of gold dot, ring, and corpuscle arrays from block copolymer templates via a simple modification of surface energy*. Nanoscale, 2011. **3**(12): p. 5007-5012.
 119. Rodwogin, M.D., et al., *Nanoscale Rings from Silicon-Containing Triblock Terpolymers*. Acs Applied Materials & Interfaces, 2012. **4**(7): p. 3550-3557.
 120. Chuang, V.P., et al., *Self-Assembled Nanoscale Ring Arrays from a Polystyrene-*b*-polyferrocenylsilane-*b*-poly(2-vinylpyridine) Triblock Terpolymer Thin Film*. Advanced Materials, 2009. **21**(37): p. 3789-3793.
 121. Liu, Y., et al., *Formation of periodic nanoring arrays on self-assembled PS-*b*-PMMA film under rapid solvent-annealing*. Nanoscale, 2010. **2**(10): p. 2065-2068.
 122. Wang, L., et al., *Gold nanoring arrays from responsive block copolymer templates*. Chemical Communications, 2009. **0**(25): p. 3798-3800.
 123. Zu, X., et al., *In situ fabrication of ordered nanoring arrays via the reconstruction of patterned block copolymer thin films*. Chemical Communications, 2010. **46**(42): p. 7927-7929.
 124. Chao, C.-C., et al., *Silicon oxy carbide nanorings from polystyrene-*b*-polydimethylsiloxane diblock copolymer thin films*. Soft Matter, 2010. **6**(15): p. 3582-3587.
 125. Lu, G., et al., *Fabricating Ordered Two-Dimensional Arrays of Polymer Rings with Submicrometer-Sized Features on Patterned Self-Assembled Monolayers by Dewetting*. Advanced Materials, 2002. **14**(15): p. 1049-1053.
 126. Clendenning, S.B., et al., *Ordered 2D arrays of ferromagnetic Fe/Co nanoparticle rings from a highly metallized metallopolymer precursor*. Journal of Materials Chemistry, 2004. **14**(11): p. 1686-1690.
 127. George, A. and J.E. ten Elshof, *Sub-50 nm patterning of functional oxides by soft lithographic edge printing*. Journal of Materials Chemistry, 2012. **22**(19): p. 9501-9504.
 128. Zhang, L., H.-Y. Si, and H.-L. Zhang, *Highly ordered fluorescent rings by "breath figures" on patterned substrates using polymer-free CdSe quantum dots*. Journal of Materials Chemistry, 2008. **18**(23): p. 2660-2665.
 129. Ren, Z.Y., et al., *Building cavities in microspheres and nanospheres*. Nanotechnology, 2009. **20**(6).
 130. Sun, F., et al., *Morphology Control and Transferability of Ordered Through-Pore Arrays Based on the Electrodeposition of a Colloidal Monolayer*. Advanced Materials, 2004. **16**(13): p. 1116-1121.
 131. Meng, T., et al., *Fabrication of Metallic Split-Ring Arrays for Metamaterials Using Silica Particle Templates Anchored on a Silicon Substrate*. Japanese Journal of Applied Physics, 2008. **47**(10): p. 8109-8112.

132. Sun, F.Q., J.C. Yu, and X.C. Wang, *Construction of size-controllable hierarchical nanoporous TiO₂ ring Arrays and their modifications*. Chemistry of Materials, 2006. **18**(16): p. 3774-3779.
133. Zhu, D., et al., *Fabrication of Heterogeneous Double-Ring-Like Structure Arrays by Combination of Colloidal Lithography and Controllable Dewetting*. Langmuir, 2012. **28**(5): p. 2873-2880.
134. Li, Z., et al., *Fabrication of size-controllable Fe₂O₃ nanoring array via colloidal lithography*. Nanoscale, 2011. **3**(7): p. 2743-2747.
135. Sun, F., et al., *Morphology-Controlled Growth of Large-Area Two-Dimensional Ordered Pore Arrays*. Advanced Functional Materials, 2004. **14**(3): p. 283-288.
136. Chen, X., et al., *Versatile Nanopatterned Surfaces Generated via Three-Dimensional Colloidal Crystals*. Advanced Materials, 2003. **15**(17): p. 1413-1417.
137. Manso Silvan, M., et al., *Aminofunctionalization and sub-micrometer patterning on silicon through silane doped agarose hydrogels*. Journal of Materials Chemistry, 2009. **19**(29): p. 5226-5233.
138. Wang, Y., et al., *A modified nanosphere lithography for the fabrication of aminosilane/polystyrene nanoring arrays and the subsequent attachment of gold or DNA-capped gold nanoparticles*. Journal of Materials Chemistry, 2004. **14**(24): p. 3488-3494.
139. Dong, W., et al., *Fabrication of two-dimensional arrays of micron-sized gold rings based on preferential nucleation at reentrant sites*. Chinese Physics Letters, 2008. **25**(8): p. 2957-2960.
140. Ahn, W. and D.K. Roper, *Periodic Nanotemplating by Selective Deposition of Electroless Gold Island Films on Particle-Lithographed Dimethyldichlorosilane Layers*. ACS Nano, 2010. **4**(7): p. 4181-4189.
141. Liao, W.-S., et al., *Templating Water Stains for Nanolithography*. Nano Letters, 2007. **7**(8): p. 2452-2458.
142. Cherniavskaya, O., et al., *Edge Transfer Lithography of Molecular and Nanoparticle Materials*. Langmuir, 2002. **18**(18): p. 7029-7034.
143. Cai, Y., et al., *Deflected Capillary Force Lithography*. ACS Nano, 2012. **6**(2): p. 1548-1556.
144. Wang, T., et al., *Morphology-controlled fabrication of elliptical nanoring arrays based on facile colloidal lithography*. Journal of Materials Chemistry C, 2013. **1**(6): p. 1122-1129.
145. Sun, Z., et al., *Three-Dimensional Colloidal Crystal-Assisted Lithography for Two-Dimensional Patterned Arrays*. Langmuir, 2007. **23**(21): p. 10725-10731.
146. Yu, J., Q.F. Yan, and D.Z. Shen, *Co-Self-Assembly of Binary Colloidal Crystals at the Air-Water Interface*. Acs Applied Materials & Interfaces, 2010. **2**(7): p. 1922-1926.
147. Fitch, R.M. *Latex particle nucleation and growth*. in ACS Symposium Series. 1981. ACS Publications.
148. Ugelstad, J., M. El-Aasser, and J. Vanderhoff, *Emulsion polymerization: initiation of*

- polymerization in monomer droplets*. Journal of Polymer Science: Polymer Letters Edition, 1973. **11**(8): p. 503-513.
149. Fitch, R. and C.H. Tsai, *Particle Formation in Polymer Colloids, III: Prediction of the Number of Particles by a Homogeneous Nucleation Theory*, in *Polymer Colloids*, R. Fitch, Editor. 1971, Springer US. p. 73-102.
 150. Ottewill, R. and J. Shaw, *Studies on the preparation and characterisation of monodisperse polystyrene latices*. Kolloid-Zeitschrift und Zeitschrift für Polymere, 1967. **218**(1): p. 34-40.
 151. Shim, S.-E., et al., *Size control of polystyrene beads by multistage seeded emulsion polymerization*. Journal of Applied Polymer Science, 1999. **71**(13): p. 2259-2269.
 152. Walters, D.A., *A stable transitional flow pattern in the surface tension driven spreading of ethanol-water solutions*. Langmuir, 1990. **6**(5): p. 991-994.
 153. Reincke, F., et al., *Understanding the self-assembly of charged nanoparticles at the water/oil interface*. Physical Chemistry Chemical Physics, 2006. **8**(33): p. 3828-3835.
 154. Reincke, F., et al., *Spontaneous Assembly of a Monolayer of Charged Gold Nanocrystals at the Water/Oil Interface*. Angewandte Chemie International Edition, 2004. **43**(4): p. 458-462.
 155. Pieranski, P., *Two-Dimensional Interfacial Colloidal Crystals*. Physical Review Letters, 1980. **45**(7): p. 569-572.
 156. Kralchevsky, P.A. and N.D. Denkov, *Capillary forces and structuring in layers of colloid particles*. Current Opinion in Colloid & Interface Science, 2001. **6**(4): p. 383-401.
 157. Kajiyama, T., K. Tanaka, and A. Takahara, *Surface Molecular Motion of the Monodisperse Polystyrene Films*. Macromolecules, 1997. **30**(2): p. 280-285.
 158. Tanaka, K., A. Takahara, and T. Kajiyama, *Rheological Analysis of Surface Relaxation Process of Monodisperse Polystyrene Films*. Macromolecules, 2000. **33**(20): p. 7588-7593.
 159. Morton, M., S. Kaizerman, and M.W. Altier, *Swelling of latex particles*. Journal of Colloid Science, 1954. **9**(4): p. 300-312.
 160. Zhao, Q., et al., *Fabrication of ordered nanoring arrays via the footprint of a polymer nanosphere monolayer*. RSC Advances, 2013. **3**(26): p. 10301-10308.
 161. Krasnoslobodtsev, A.V. and S.N. Smirnov, *Effect of Water on Silanization of Silica by Trimethoxysilanes*. Langmuir, 2002. **18**(8): p. 3181-3184.
 162. Allen, G.C., et al., *Macro-, micro- and nano-investigations on 3-aminopropyltrimethoxysilane self-assembly-monolayers*. Thin Solid Films, 2005. **483**(1-2): p. 306-311.
 163. Fadeev, A.Y. and T.J. McCarthy, *Self-Assembly Is Not the Only Reaction Possible between Alkyltrichlorosilanes and Surfaces: Monomolecular and Oligomeric Covalently Attached Layers of Dichloro- and Trichloroalkylsilanes on Silicon*. Langmuir, 2000. **16**(18): p. 7268-7274.
 164. Mittal, K.L., *Silanes and Other Coupling Agents*. Vol. 4. 2007.

165. Trens, P. and R. Denoyel, *Adsorption of (γ -aminopropyl) triethoxysilane and related molecules at the silica/heptane interface*. Langmuir, 1996. **12**(11): p. 2781-2784.
166. Kurth, D.G. and T. Bein, *Thin films of (3-aminopropyl) triethoxysilane on aluminum oxide and gold substrates*. Langmuir, 1995. **11**(8): p. 3061-3067.
167. Tsai, H.-J. and Y.-L. Lee, *Manipulation ordered and close-packed nanoparticle monolayers at air/liquid interface coupling Langmuir-Blodgett and self-assembly techniques*. Soft Matter, 2009. **5**(15): p. 2962-2970.
168. Park, S., et al., *Transition Metal-Coated Nanoparticle Films: Vibrational Characterization with Surface-Enhanced Raman Scattering*. Journal of the American Chemical Society, 2002. **124**(11): p. 2428-2429.
169. Neogi, P., *Diffusion in polymers*. Vol. 32. 1996: CRC Press.
170. Dann, J.R., *Forces involved in the adhesive process: II. Nondispersion forces at solid-liquid interfaces*. Journal of Colloid and Interface Science, 1970. **32**(2): p. 321-331.
171. Ober, R., et al., *Study of the surface tension of polymer solutions: theory and experiments. Good solvent conditions*. Macromolecules, 1983. **16**(1): p. 50-55.
172. Scott, H.J. and J. Hildebrand, *The solubility of nonelectrolytes*. New York: Reinhold, 1949.
173. Hiorns, R., *Polymer Handbook, 4th edn, Edited by J Brandup, EH Immergut and EA Grulke, Associate Editors A Abe and DR Bloch, John Wiley and Sons, New York, 1999, pp 2250, price £210 ISBN 0-471-16628-6*. Polymer International, 2000. **49**(7): p. 807-807.
174. Burke, J., *Solubility parameters: theory and application*. 1984.
175. Suh, K.W. and D.H. Clarke, *Cohesive energy densities of polymers from turbidimetric titrations*. Journal of Polymer Science Part A-1: Polymer Chemistry, 1967. **5**(7): p. 1671-1681.
176. Mark, J.E., *Polymer Data Handbook (2nd Edition)*. Oxford University Press.
177. Ng, E.C.H., K.M. Chin, and C.C. Wong, *Controlling Inplane Orientation of a Monolayer Colloidal Crystal by Meniscus Pinning*. Langmuir, 2011. **27**(6): p. 2244-2249.
178. Bartlett, P. and A. Campbell, *Three-dimensional binary superlattices of oppositely-charged colloids*. arXiv preprint cond-mat/0505001, 2005.

APPENDIX: Publications and Conferences

Qin ZHAO, Bing LENG, Linda Yong Ling WU, and Chee Cheong WONG, “Fabrication of Ordered Nanoring Array via the Footprint of a Polymer Nanosphere Monolayer”, *RSC Advances*, 2013, 3, 10301

Qin ZHAO, Puqun WANG, and Chee Cheong WONG, “Effects of Ethanol and Three-phase Contact Angle on Gold Nanoparticle Adsorption at Water/Toluene Interface”, *Nanoscience and Nanotechnology Letters*, 2012, 4, 1140.

Qin ZHAO, Eric Chin Hong NG, Husen Kartasasmita KANG, and Chee Cheong WONG, “Real Time Visualization of Surfactant Effects on Colloidal Self-assembly”, *International Journal of Nanoscience*, 2010, 9, 113.

Qin ZHAO, Bing LENG, Chee Cheong WONG, *EMRS (European Materials Research Society)* 2013, Oral Presentation

Qin ZHAO, Puqun WANG, Chee Cheong WONG, *6th Thin Films (International Conference on Technological Advances of Thin Films & Surface Coatings)* 2012, Oral Presentation

Qin ZHAO, Husen Kartasasmita KANG, Chee Cheong WONG, *ICMAT (International Conference on Materials for Advanced Technologies)* 2011, Oral presentation

Qin ZHAO, Puqun WANG, Chee Cheong WONG, *5th Thin Films (International Conference on Technological Advances of Thin Films & Surface Coatings)* 2010, Oral Presentation

Qin ZHAO, Eric Chin Hong NG, Chee Cheong WONG, *ICMAT (International Conference on Materials for Advanced Technologies)* 2009, Oral presentation